

**St. Lawrence River Sediment  
Chemical Assessment 1997,  
Cornwall, Ontario**

**September 1999**



Ministry of the  
Environment



# St. Lawrence River Sediment Chemical Assessment 1997, Cornwall, Ontario

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## FOREWORD

Since 1970 there have been several sediment surveys in the St. Lawrence River along the Cornwall waterfront to delineate the extent of sediment contamination and to associate these contaminants with local point sources. These surveys identified mercury contaminated sediment extending downstream from Domtar Fine Paper Ltd. and ICI Forest Products (formerly called CIL), and adjacent to, and downstream of the former Courtaulds Fibres Canada property (herein referred to as Courtaulds) (MOE 1979; Kauss et al. 1988; Anderson 1990; Richman 1994; Richman 1996). Sediment samples collected in both these areas since 1970 exceeded the "severe effect level" (SEL) of the Ontario Sediment Quality Guidelines for mercury and sediment collected downstream of Courtaulds also exceeded the SEL for lead, copper and zinc.

This project was put forward by the Cornwall Sediment Management Plan committee to provide information for the development of a plan to address contaminated sediment in the St. Lawrence River at Cornwall, Ontario. The data from this report will be integrated with additional information generated by related studies in the St. Lawrence River so that sediment management options can be proposed.

This report has been prepared under the auspices of the Canada-Ontario Great Lakes Remedial Action Plan Program. Financial support for the sampling projects, data analysis and report writing was provided by Environment Canada (EC) and the Ontario Ministry of Environment (MOE). This was a collaborative project between MOE (Environmental Monitoring and Reporting Branch and Eastern Region) and EC (Environmental Conservation Branch; Restoration Program Division and National Water Research Institute).

The report presents the findings, recommendations, and conclusions of the author, and does not necessarily represent the views or policies of the supporting agencies.

For additional technical reports or information on the St. Lawrence River Remedial Action Plan (RAP), contact the Ontario Ministry of Environment at 133 Dalton Road, Kingston Ontario, K7L 4X6.

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Laboratory sample analyses were performed by EC National Laboratory for Environmental Testing (NLET) and MOE Laboratory Services Branch.

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## SUMMARY

The St. Lawrence River near Cornwall, Ontario was designated as a Great Lakes Area of Concern (AOC) in 1985 by the International Joint Commission in part because of contaminated sediment located along the north shore of the Cornwall waterfront. Sediment surveys along the waterfront since 1970 showed sediment concentrations greater than the "severe effect level" (SEL) of the Ontario Sediment Quality Guidelines for mercury extending downstream from Domtar Fine Paper Ltd. (herein referred to as Domtar) and ICI Forest Products (formerly called CIL). Sediment downstream of the former Courtaulds Fibres Canada facility (herein referred to as Courtaulds) had concentrations greater than the SEL for mercury, lead, copper and zinc (MOE, 1979; Kauss et al. 1988; Anderson 1990; Richman 1994; Richman 1996). As such, a Remedial Action Plan (RAP) to improve the local conditions of the aquatic environment identified the need to address the issue of sediment contamination along the Cornwall waterfront (Dreier et al. 1997).

Prior to the development of a sediment management strategy for the waterfront more recent information was required on the local sediment quality to identify areas of contaminated sediment which may require consideration for remediation.

The objectives of the 1997 sediment survey were as follows:

- (1) *to determine if concentrations of various metals and organics in sediment located in a deposition zone about 1.4 km downstream of the Domtar/ICI diffuser and adjacent to the north east side of Cornwall Island exceed the Provincial Sediment Quality Guidelines "severe effect level" (SEL) and "lowest effect level" (LEL).*
- (2) *to update sediment quality information downstream of the Courtaulds facility using sampling sites based on a 1994 MOE sediment survey.*

Sediment was collected from 24 stations using a mini-box corer (Figure 1). At each station 10 cm cores (using 10 cm core tubes, diameter-6.5 cm) and surface samples (top 3 cm) were collected from the mini-box corer. Sediment samples were analysed for trace metals, phosphorus, % TOC and particle size.

All sediment samples collected along the Cornwall waterfront (north shore of the channel) exceeded the LEL for mercury and 46 % of the samples exceeded the SEL. The highest concentrations of mercury in 10 cm core samples (19.5  $\mu\text{g/g}$  and 11.2  $\mu\text{g/g}$ ) were detected in sediment collected downstream of Courtaulds at stations CS131 and CS128 respectively. In contrast, all stations on the south side of the channel had mercury concentrations less than the LEL indicating that this area was not contaminated. These results were consistent with previous sediment surveys (MOE 1979; Kauss et al. 1988; Anderson 1991; Richman 1994, 1996).

A comparison of metal sediment concentrations in samples (10 cm cores) collected from the north side of the north channel showed that median concentrations of cadmium (0.89  $\mu\text{g/g}$ ), nickel (24  $\mu\text{g/g}$ ) and TOC (2.5%) were similar to concentrations detected on the south side of the channel (1.02  $\mu\text{g/g}$ , 30.8  $\mu\text{g/g}$  and 2.5% respectively). Median concentrations of copper and lead were also similar on both sides of the channel, however, the range in concentrations for copper and lead was higher on the north shore than the south. Stations with the highest concentrations of copper and lead were located downstream of Courtaulds. Median concentrations of zinc (186  $\mu\text{g/g}$ ) were higher on the north shore compared with the south shore (136  $\mu\text{g/g}$ ) indicating enrichment for this parameter as would be expected based on historical discharge patterns from Courtaulds and confirmed in previous sediment surveys (Kauss et al. 1988; Anderson 1991; Richman 1994, 1996).

A comparison of particle size corrected data from Cornwall with data from an upstream reference area showed that the sediment along the north side of the channel was enriched with zinc at all stations and with lead and copper at selected stations downstream of Courtaulds which historically discharged these metals (MOE 1992a). Particle size corrected data showed that all stations along the north shore (downstream of the Domtar/ICI diffusers and downstream of Courtaulds) were enriched with mercury compared with the upstream reference area. All three industries were known dischargers of mercury (MOE 1979; MOE 1992a&b). Particle size corrected data also showed the same pattern described above (i.e. higher concentrations on the north shore), when comparing concentrations of mercury, lead, zinc and copper in sediment from the north side relative to sediment concentrations on the south side of the channel, confirming that the south side of the channel was not impacted by local industrial sources.

A statistical examination of the relationships among contaminant concentrations at all sampling locations (Principal Component Analysis), grouped Hg, Pb, Zn and Cu together indicating that these parameters were correlated with one another (i.e. exhibited similar patterns of variation from one location to another). Stations with high Hg, Pb, Zn and Cu sediment concentrations were also grouped together and were all located downstream of Courtaulds which historically discharged these metals.

An assessment of contaminant concentrations in the bottom 10 cm of selected cores confirmed that stations about 1.4 km downstream of the Domtar/ICI diffusers were historically contaminated by mercury. These results were consistent with data from the 1970's (MOE 1979; Kauss et al. 1988). The high concentrations (4.63  $\mu\text{g/g}$  and 13.70  $\mu\text{g/g}$ ) were likely due to upstream discharges of mercury from the Fly Creek sewer and from the Domtar/ICI diffuser when it came on line in 1972 and replaced the Fly Creek sewer. Surface samples from these stations show some enrichment of mercury relative to the south side of the north channel (which was not impacted by local sources) and relative to upstream reference stations, however, present concentrations were below the SEL and lower than contaminated sites downstream of Courtaulds.

An analysis of covariance (ANCOVA) was used to compare metal concentrations in the 1997 surface sediment samples (top 3 cm) with the concentrations in the 1997 core samples (top 10 cm) collected from the same stations to review changes in contaminant concentrations over time. This was based on the assumption that the top 3 cm of sediment represented the most recent sediment quality. The ANCOVA found that there was no significant difference in metal concentrations in the surface samples compared with the 10 cm core top samples for all the parameters tested with the exception of cadmium and chromium which showed weak statistical differences. This suggests that sediment quality has not changed at the surface relative to the underlying sediment. However, sediment mixing due to bioturbation and other physical processes within the river may make any change in sediment quality too small to measure within the top 10 cm.

## CONCLUSIONS

*1) Surface sediment located in the deposition zone about 1.4 km downstream of the Domtar/ICI diffuser has mercury concentrations that were greater than the LEL but less than the SEL. Sediment at this site was historically contaminated with mercury. This is evident from high concentrations in sediment collected from the bottom of the core (4.63 ug/g and 13.70 ug/g) relative to mercury concentrations in sediment at the top of the core sample (1.19 ug/g and 1.71 ug/g respectively) . This area was not contaminated with other metals.*

*2) Sediment located adjacent to the north east side of Cornwall Island was not contaminated with metals.*

*3) The highest concentrations of mercury, lead, copper and zinc in the study area were located downstream of the former Courtaulds Fibre Canada facility. Remediation of contaminated sediment, if considered, should be focussed in this deposition zone. Sampling sites in this area could be used for future monitoring to assess changes in sediment quality with time.*



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## INTRODUCTION

Since 1970 there have been several sediment surveys in the St. Lawrence River along the Cornwall waterfront to delineate the extent of sediment contamination and to associate these contaminants with local point sources. These surveys identified mercury contaminated sediment extending downstream from Domtar Fine Paper Ltd. (herein referred to as Domtar) and ICI Forest Products (formerly called CIL), and adjacent to, and downstream of the former Courtaulds Fibres Canada property (herein referred to as Courtaulds) (MOE 1979; Kauss et al. 1988; Anderson 1990; Richman 1994; Richman 1996) (Figure 1). Sediment samples collected in both these areas since 1970 exceeded the "severe effect level" (SEL) of the Ontario Sediment Quality Guidelines for mercury and sediment collected downstream of Courtaulds also exceeded the SEL for lead, copper and zinc.

Local industries located upstream of the areas with contaminated sediment have discharged mercury, zinc, lead and copper to the St. Lawrence River. Based on a six month average loading calculation from October 1989 to March 1990, Courtaulds Fibres Canada was one of the largest dischargers of zinc in Ontario. Courtaulds discharged 399.95 kg/d of zinc, 2.25 kg/d of lead, 0.726 kg/d of copper and 0.120 kg/d of mercury (MOE 1992a-unpublished data). Historically Courtaulds discharged higher concentrations of lead because of the corrosion of their lead pipes and their use of lead as a lining in their acid storage tanks. Prior to its closure, the company had almost completely replaced its lead pipes and tank lining with plastic products reducing the concentrations of lead that were discharged to the river, however, the company still discharged higher lead concentrations than the other local upstream sources in the study area (MOE 1992a,b). Courtaulds also decreased its mercury loadings to the river due to changes in their distributors of caustic soda and sulphuric acid which were contaminated with mercury, however, concentrations in their effluent were still higher than other local sources when data was collected in 1989. In November 1992, Courtaulds Fibres Canada closed its facility in Cornwall, Ontario.

Domtar discontinued its use of mercurial slimicides in 1964 (MOE 1979) and according to six month average loading calculation from January 1990 to June 1990, Domtar discharged 5.7 kg/d of zinc and 0.843 kg/d of copper (MOE 1991). ICI significantly reduced its loadings of mercury to water in the early 1970s to an average of 23 kg/yr (0.063 kg/d) from a high of 590 kg/yr (MOE 1979; MOE 1992b). ICI discharged insignificant amount of zinc (0.111 kg/d) relative to Courtaulds and 0.178 kg/d of lead and 0.082 kg/d of copper. ICI closed its Cornwall chlor-alkali plant in 1995.

The St. Lawrence River near Cornwall, Ontario was designated as a Great Lakes Area of Concern (AOC) in 1985 by the International Joint Commission in part because of the mercury contaminated sediment. As such, a Remedial Action Plan (RAP) to improve the local conditions

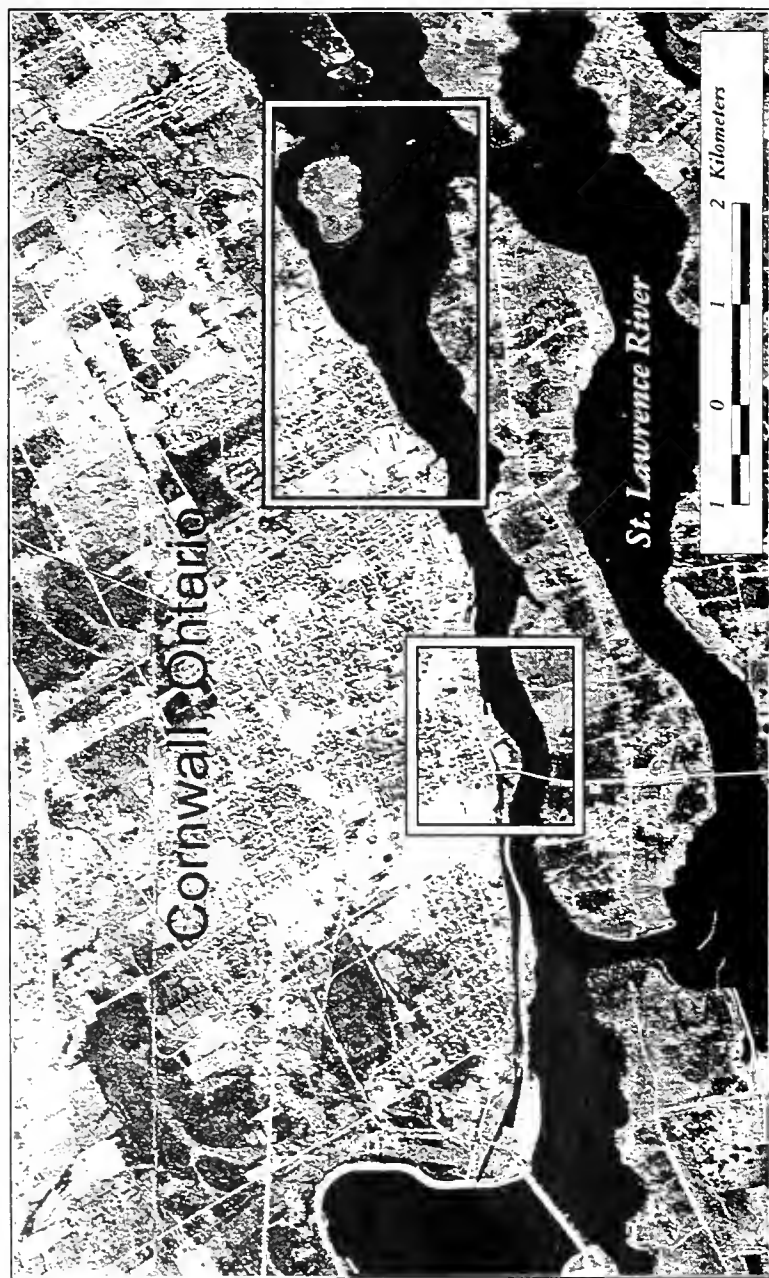


Figure 1: Study area and sampling sites.

of the aquatic environment identified the need to address the issue of sediment contamination along the Cornwall waterfront (Dreier et al. 1997).

Prior to the development of a sediment management strategy for the waterfront more recent information was required on the sediment quality located in a deposition zone about 1.4 km downstream of Domtar and ICI. As well, this survey provided an opportunity to reassess the sediment quality of a deposition zone on the south side of the north channel adjacent to Cornwall Island identified through the use of the RoxAnn<sup>TM</sup> seabed classification system (Rukavina 1997). This area was sampled previously by the Ministry of Environment (MOE) and was shown not to be contaminated by local point source discharges (MOE, 1979; Kauss et al. 1988; Anderson 1990).

The objectives of the 1997 sediment survey were as follows:

- (1) *to determine if concentrations of various metals and trace organics in sediment located in a deposition zone about 1.4 km downstream of the Domtar/ICI diffuser and adjacent to the north east side of Cornwall Island exceed the Provincial Sediment Quality Guidelines "severe effect level" (SEL) and "lowest effect level" (LEL).*
- (2) *to update sediment quality information downstream of the former Courtaulds Fibres Canada facility using sampling sites based on a 1994 MOE sediment survey.*

Accordingly, sediment was collected jointly by MOE and Environment Canada (EC) from 24 stations in October 1997, and samples were analysed for a range of contaminants and physical parameters.

## **METHODOLOGY**

### **Sampling Stations and Field Methods**

Sediment was collected from 24 stations using a mini-box corer from October 21 to 23, 1997 (Figure 1). Results from detailed acoustic mapping of bottom sediment type, grain-size types and sediment thickness using a RoxAnn<sup>TM</sup> seabed classification system were used to choose sampling stations (Rukavina 1997). Appendix A provides details on exact station locations. A boat equipped with RoxAnn<sup>TM</sup> was used to identify areas with sufficient soft sediment for efficient use of the mini-box corer. These sites were marked with floats and the exact northing and easting were recorded using a differential Global Positioning System (DGPS). The sampling vessel then returned to these locations for sediment sample collection. An attempt was made to return to sites previously sampled in 1994 but deviations in the location of some of the stations from the 1994 survey grid were required to meet the needs of the mini-box corer.

At each station two 10 cm cores (using 10 cm core tubes, diameter-6.5 cm) were collected from the mini-box corer (38 x 38 x 46 cm), homogenized in a hexane rinsed glass tray using a stainless steel hexane rinsed spatula and split into three pre-cleaned 500 mL amber sample jars with Teflon lined lids. Care was taken to rinse all mixing tools and tray with water and hexane between sampling stations to avoid cross contamination. Sediment in one jar was analysed for organics, one jar for trace metals, TOC and particle size analysis, and one jar for mercury analysis. Three surface samples (top 3 cm) were collected from each station by removing sediment from the mini-box corer using a 3 cm square surface sampler. These were homogenized and placed in one jar for metals (including mercury), TOC and particle size analysis. All samples were frozen at -20°C until samples analysis.

At six stations (three stations about 1.4 km downstream of Domtar/ICI and three stations located in the deposit on the south side of the north channel), two full length cores were collected from the box corer (maximum depth of box-corer: 46 cm) to assess contamination at the bottom of the cores as well as within the top 10 cm of the cores. At these stations the top 10 cm from each full length core was sectioned and homogenized (rather than using the 10 cm core tubes) and the bottom 10 cm of the two cores were sectioned and then homogenized. The samples were split into sample jars as described above. The total lengths of these cores are provided in Appendix A.

QA/QC samples were collected at five stations to evaluate sample variability within the mini-box corer. First routine samples were collected at these stations as described above. Then a second mini-box core sample was collected and six 10 cm cores were removed. Pairs of 10 cm cores were homogenized per box corer sample resulting in a total of three replicate samples for “within box” variability analysis. This procedure was performed at four of the five QA/QC stations. The samples from three of the stations were analysed for the parameters described in Table 1, and the samples from the fourth station were archived. The fifth QA/QC station was used to evaluate laboratory analytical precision and variability due to sample handling and collection. Two of the three replicate samples collected at this station were each split three ways. The three sub-samples from each replicate were analysed for metals (excluding mercury), TOC and particle size. The third single replicate was analysed for all the parameters listed in Table 1.

In order to assess temporal trends between 1997 and 1994 data, an interlaboratory comparison of metals and particle size analysis was required since the EC lab was responsible for the 1997 analysis and the MOE lab analysed the 1994 sediment samples. At nine stations sediment samples were split for interlaboratory comparisons between MOE and EC. Two 10 cm cores were homogenized and split into two samples. Results were available for eight stations due to breakage of one sample container in transit.

### **Contaminant Analysis of Sediment**

Sediment samples were analysed for particle size, a complete ICP metal scan, total phosphorus, % TOC and polycyclic aromatic hydrocarbons (PAHs). For selected stations, polychlorinated biphenyls (PCBs) and organochlorine pesticides were also analysed. Parameters discussed in this

report include only trace metals, nutrients and particle size. A complete list is provided in Table 1. Sediment analyses for PCBs and PAHs were not completed when this report was written.

Table 1: Sediment samples were analysed for the following parameters:	
Total Organic Carbon (TOC)	
Total Phosphorus (TP)	
Chromium	Cadmium
Mercury	Manganese
Lead	Zinc
Aluminum	Nickel
Copper	Iron
Particle Size	

Sediment samples were analysed by EC at the National Laboratory for Environmental Testing (NLET). Freeze dried sediment screened at 2 mm to remove bulk debris was weighed to 0.5 grams in a PFA Teflon vessel; 9 mL of nitric acid, 2 mL of hydrochloric acid and 1 mL of hydrogen peroxide were added. The vessel was sealed, placed in a high pressure microwave oven and the sediment was allowed to digest at 200 °C for at least 15 minutes. The digests were brought to a final volume of 100 mL with deionized water and stored in FEP Teflon bottles. The procedure was based on EPA Method 3052 which describes the digestion of siliceous and organically based matrices. This study was not concerned with the extraction of silica-bound metals, hence hydrofluoric acid was not added to the extraction mixture. Al, Ba, Cr, Cu, Fe, Mn, P, Pb, Sr, Ti, V, Zn, Ca and Mg were analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES). After a ten-fold dilution of the digest, lower concentration elements, Be, Cd, Co, Li, Mo, Ni, Rb, Tl, La and U were measured by inductively coupled plasma-mass spectrometry (ICP-MS). One gram of wet sediment was digested under the same microwave conditions, and Hg was analysed by cold vapour atomic absorption spectrometry (CVAAS). The Hg results were reported on a dry weight basis after the determination of the moisture content.

Particle size was analysed by the Sieve and Sedigraph method. Sand and coarse fractions were determined by using electromagnetic 8 inch brass sieves while size fractions less than 63 µm were measured using the 5100 x-ray analyser. The two data sets were merged to provide the total particle size analysis.

For split samples analysed at the MOE Rexdale laboratory all laboratory analytical procedures for contaminants in sediment followed the methodology outlined in the Handbook of Analytical Methods for Environmental Samples (MOE 1983). Procedural updates for metals analysis are

provided in MOE 1989a & b. Procedural updates for nutrient analysis and TOC are provided in MOEE 1995a & b.

## **Data Analysis**

### **Identification of Contaminated Sediment**

Sediment contaminant concentrations were compared with the Provincial Sediment Quality Guidelines (Persaud et al. 1992). These guidelines describe three "effect" levels for different contaminants in terms of potential effects on the benthic community: (1) the no observed effect level; (2) the lowest effect level (LEL) which is the level of sediment contamination that can be tolerated by the majority of benthic organisms (concentrations greater than this level indicate that the benthic communities in these areas may be impaired); and (3) the severe effect level (SEL) which is the sediment concentration of a compound that is expected to be detrimental to the majority of benthic species. Sediment contaminant concentrations may exceed the LEL and/or the SEL with no apparent impact on the benthic community, nevertheless these guidelines serve as a point of reference to investigate the extent of sediment contamination within the study area and to compare the relative contamination with other locations.

To compare sediment contaminant concentrations between the north and south side of the channel the median and range in contaminant concentrations were presented.

A principal components analysis using the Numerical Taxonomy and Multivariate Analysis System (PCA) (NTSYS-pc; Rohlf 1988) was used to reduce the data onto three components representing the variables that best correlate with one another and explain the major sources of variation in sediment quality among the 24 stations. The PCA included the 3 cm surface samples and surface core samples (10 cm) from all stations. All data were log transformed with the exception of the particle size data. The PCA was repeated using non-transformed data, using only north shore data and with only the core data. The overall conclusions interpreted from the analysis remained the same for all scenarios.

### **Particle Size Correction Method**

Trace elements tend to accumulate and bind to the clay/silt sediment fraction represented by particle sizes of less than 63  $\mu\text{m}$  (Forstner and Wittmann 1983; Krumgalz et al. 1992).

Consequently, the heterogenous nature of the sediment in the St. Lawrence River makes it necessary to adjust trace element concentrations for the different particle size distributions at the various sampling stations in order to compare contaminant concentrations between stations if the effect of depositional environments are to be diminished and trace metal contaminant sources are to be inferred. There are several methods frequently used to correct for depositional environments and hence particle size differences between stations (Forstner and Wittmann 1983; Krumgalz et al. 1992).

The approach taken in this report was to normalize the anthropogenic trace metal results to a "conservative" element such as aluminum (i.e. an element that is not believed to be locally anthropogenic in origin). The ratio of the other metals to aluminum should remain constant across a gradient of particle sizes unless there is an enrichment of the other metal (Forstner 1990). Results from the 1994 survey showed some enrichment of aluminum in sediment samples within the study area (relative to the upstream reference area that was used for the comparison of sediment quality), likely due to anthropogenic atmospheric sources in Massena, (Richman 1996). To determine the appropriateness of this method of correction, aluminum concentrations measured in the surface sediment were compared with concentrations measured in the bottom of core samples (expected to represent historical aluminum concentrations), collected from the same locations. Using the 1994 data set, this type of comparison showed there was less than a 30% difference between surface and core bottom aluminum concentrations. This difference was within the range of variability for replicate core samples and suggests little change in aluminum concentrations over time. Accordingly, a correction for particle size was valid using this method although the potential exists to underestimate the local enrichment of other metals.

To further complement the results obtained from this correction method, the data were also corrected by normalizing metal concentrations at all stations to a fine particle ( $<63\ \mu\text{m}$ ) content of 74%. This involved the multiplication of the contaminant concentration at a site by 74% and then dividing by the actual percent silt plus clay for the station. This percentage (74%) was chosen since it was the median value for the particle size distribution for all samples collected in the study area. Another commonly used option would have been to normalize the concentration of contaminants to a fine particle content of 100% however this method has a tendency to produce inordinately high metal concentrations at stations high in sand.

To determine if the north channel downstream of the major point sources in Cornwall was contaminated with metals, a comparison was made between particle size corrected data from both this area and sediment data collected from Maitland, upstream of Cornwall. Results from a sediment survey in 1991 in the Maitland area where 48 stations were sampled along 11 transects were used for the comparison (Richman and Townsend 1997). The extensive (116 samples in total) 1991 survey concluded that the St. Lawrence River at Maitland was not severely contaminated with metals or nutrients and concentrations of contaminants at most sites were consistent with background stations making this an appropriate reference area. Details on sampling methods and the study area are provided in Richman and Townsend (1997).

Accordingly, all the metal data from Maitland were corrected for particle size by calculating the ratio of the concentration of a particular metal to the concentration of aluminum. The mean, and upper and lower 95% confidence intervals were calculated for Maitland and then compared with the normalized Cornwall data. All metal:Al ratios at Cornwall stations greater than the upper confidence limit for reference area metal:Al ratios were identified as being enriched with the particular parameter. The same procedure was followed using the correction method of normalizing the data to 74% fines.

## **Statistical Approach to Assess Temporal Changes in Sediment Contaminant Concentrations**

Since the EC lab was responsible for the 1997 analysis and the MOE lab analysed the 1994 sediment samples, an inter-lab comparison of metals and particle size analysis was required in order to assess temporal trends. The inter-lab comparison was conducted through the splitting of 8 samples from different locations for analysis by each lab. A paired t-test was used to compare the metals data generated by the two laboratories. The results from the paired t-test were then used to identify the parameters appropriate for the “between year” comparison to determine if contaminant concentrations in sediment had changed over time.

The comparison of 1994 and 1997 data corrected for particle size from six stations was made with a paired t-test by grouping stations within a sampling year together to characterize the study area as a whole. This approach was necessary since there was only one sample at each station. Contaminant concentrations in 10 cm core samples were used for the comparison. Because of the small sample size overall (only six stations for the comparison), and the wide range in contaminant concentrations, a large change in concentration over time would be required to obtain a statistically significant difference between 1994 and 1997 data. As such the change in contaminant concentrations over time (using data that was both corrected and uncorrected for particle size), was reviewed by simple subtraction of concentrations between years to investigate general trends.

Another method to assess a change in contaminant concentrations over time was to compare concentrations of metals in the 1997 surface sediment samples (top 3 cm) with the concentrations in the 1997 core samples (top 10 cm) collected from the same stations using sampling sites from both the north and south side of the channel. This was based on the assumption that the top 3 cm of sediment consisted of more recent material than the top 10 cm. An analysis of covariance (ANCOVA) was used for the comparison between the sediment quality in these two types of samples. Particle size (% silt plus clay) was used as the covariate. The heterogeneity of slopes was tested for each parameter as a preliminary step using the SAS statistical package (SAS Institute Inc. 1988). The ANCOVA was performed for each parameter if the slopes generated for the surface samples and 10 cm core samples were not significantly different. The ANCOVA was performed on both log transformed and non-transformed data. Results from both tests were almost identical, as such results from the log transformed data were presented in this report.

## **Quality Assurance / Quality Control**

Statistical analysis and results for QA/QC samples are provided in Appendix C.

## RESULTS AND DISCUSSION

### Patterns of Sediment Contamination

Data for sediment contaminant concentrations and particle size for stations sampled in the St. Lawrence River are summarized in Table 2 & 3.

All sediment samples (10 cm cores and 3 cm surface samples) collected along the Cornwall waterfront (north shore of the channel) exceeded the LEL for mercury and 46 % of the samples exceeded the SEL (Table 2, Figure 2). These results were consistent with previous sediment surveys which found that the north side of the channel was contaminated with mercury (MOE 1979; Kauss et al. 1988; Anderson 1991; Richman 1994, 1996). In contrast, all surface samples had mercury concentrations less than the LEL on the south side of the channel. These data also confirm results from previous surveys and indicate that this area was not contaminated with mercury (MOE 1979; Kauss et al. 1988; Anderson 1991). Median concentrations of mercury in core top samples ( $3.06 \mu\text{g/g}$ ) were higher on the north shore compared with the south shore ( $0.13 \mu\text{g/g}$ ) (median concentrations and range provided in Table 4).

In general throughout the study area concentrations of cadmium, nickel, chromium, copper, lead, zinc, total phosphorus and TOC were above the LEL. A comparison of metal sediment concentrations in samples (10 cm cores) collected from the north channel showed that median concentrations of cadmium ( $0.89 \mu\text{g/g}$ ), nickel ( $24 \mu\text{g/g}$ ) and TOC (2.5%) along the north shore were similar to concentrations detected on the south side of the channel ( $1.02 \mu\text{g/g}$ ,  $30.8 \mu\text{g/g}$  and 2.5% respectively). Median concentrations of copper and lead were also similar on both sides of the channel but the range in concentrations for copper and lead was higher on the north shore (particularly downstream of Courtaulds) than the south shore (Table 4). This is consistent with data from previous surveys and the discharge patterns from local industries (MOE 1991; MOE 1992a&b). Median concentrations of zinc ( $186 \mu\text{g/g}$ ) were higher on the north shore compared with the south shore ( $136 \mu\text{g/g}$ ) as would be expected based on historical discharge patterns from Courtaulds (Kauss et al. 1988; Anderson 1991; Richman 1994, 1996) (Figure 3). Enrichment of zinc, lead and copper on the north shore downstream of Courtaulds was confirmed when data were corrected for particle size and compared with contaminant concentration upstream and on the south side of the channel.

All sediment samples from the north side of the channel (along the waterfront) were below the LEL for manganese and only one station had concentrations of iron above the LEL as compared with the south side of the channel where 57 % of the samples exceeded the LEL for manganese and all the samples exceeded the LEL for iron. Median concentrations of aluminum, iron, manganese, total phosphorus and chromium were higher on the south shore than the north. Once the sediment data were corrected for particle size there were no differences between both sides of the channel for any of these parameters.

**TABLE 2:** Metal, total phosphorus and TOC concentrations (µg/g dry weight) in sediment samples (top 10 cm core sample) collected from the St. Lawrence River, 1997. (n=1). B - bottom 10 cm of the core. S - surface sample (top 3 cm).

ENV/CAN STN #	AL µg/g	CD µg/g	CR µg/g	CU µg/g	FE µg/g	HG µg/g	MN µg/g	NI µg/g	PB µg/g	ZN µg/g	Total P µg/g	TOC %
CS105	19600	0.952	46.8	45.1	19300	1.67	295	26.8	63.3	600	761	2.926
CS109	16500	1.170	44.0	55.4	16600	<b>4.83 **</b>	252	26.2	136.0	759	638	2.872
CS109-S	19000	0.929	49.1	55.6	18600	<b>5.79 **</b>	317	26.1	156.0	673	1020	2.753
CS115	15400	1.450	41.8	57.9	16400	<b>3.66 **</b>	281	26.6	99.8	603	678	2.446
CS115-S	19400	1.080	43.7	57.6	19400	1.63	339	28.0	60.5	335	977	2.266
CS117	11500	0.608	31.4	34.9	13300	<b>2.00 **</b>	245	19.9	83.5	279	549	2.353
CS117-S	18700	0.869	40.6	42.8	18600	1.35	333	25.8	60.8	270	965	2.049
CS126	9630	0.720	23.8	26.6	12700	<b>5.20 **</b>	201	19.1	25.2	125	457	3.076
CS126-S	12200	0.424	28.5	21.8	18800	1.20	357	16.0	19.7	82	852	2.980
CS127	13500	0.473	27.8	29.4	13600	<b>4.32 **</b>	280	13.8	53.6	152	548	1.681
CS128	16800	0.637	32.7	33.6	17900	<b>11.20 **</b>	345	18.0	37.3	177	681	2.850
CS128-S	10300	0.359	25.1	21.1	15200	<b>3.44 **</b>	293	14.5	23.6	69	765	1.901
CS131	17000	0.645	33.3	42.5	18300	<b>19.50 **</b>	347	17.8	40.6	186	659	4.037
CS131-S	14900	0.758	32.0	37.6	14700	<b>14.70 **</b>	288	24.9	33.7	251	853	2.737
CS132	21800	0.949	43.8	60.9	17300	<b>6.78 **</b>	329	24.6	63.3	474	818	2.516
CS135	19000	0.984	40.3	45.5	18500	<b>3.75 **</b>	331	22.9	58.8	234	660	2.108
CS135-S	12300	0.624	27.2	19.3	14300	1.22	288	21.1	27.2	117	758	1.753
CS156	11400	0.490	26.2	16.9	14400	0.80	272	14.6	26.7	134	745	1.740
CS164	16000	0.888	48.7	59.9	17700	<b>3.09 **</b>	292	24.9	136.0	669	847	2.454
CS164-S	14800	0.795	38.4	47.3	15900	1.98	291	25.2	100.0	395	841	2.822
CS166	24400	1.220	47.5	43.2	23000	0.79	360	27.5	36.0	132	1150	3.236
CS166-B	27000	1.290	53.1	46.1	23500	0.12	328	32.8	44.2	142	1140	3.263
CS166-S	23400	1.120	45.3	43.4	22200	1.06	335	30.2	33.7	133	986	3.491
CS167	16800	0.910	37.0	39.7	16300	1.19	265	29.9	36.6	107	867	2.970
CS167-B	24700	1.420	44.0	64.4	15000	<b>4.63 **</b>	247	38.8	58.3	158	1120	6.745
CS167-S	12200	0.687	26.7	23.6	13700	1.72	239	19.5	21.9	76.9	653	2.370
CS168	17000	0.877	37.5	31.7	17000	1.71	290	24.0	38.0	102	947	1.813
CS168-B	25600	1.590	51.5	75.1	17000	<b>13.70 **</b>	286	35.9	73.6	187	1090	5.818
CS168-S	11800	0.754	26.8	21.2	13100	0.70	222	20.8	24.7	80.7	724	2.178
Lowest Effect Level		0.6	26	16	2%	0.2	460	16	31	120	600	1
Severe Effect Level **		10	110	110	4%	2	1100	75	250	820	2000	10

TABLE 2 continued:

ENV.CAN STN #	AL ug/g	CD ug/g	CR ug/g	CU ug/g	FE ug/g	HG ug/g	MN ug/g	NI ug/g	PB ug/g	ZN ug/g	Total P ug/g	TOC %
CS171	18600	0.690	36.5	31.3	19100	0.44	359	20.6	29.6	118	918	2.016
CS172	31200	1.120	58.8	46.1	26600	0.62	439	34.1	44.0	350	1120	3.340
CS173	32700	1.210	58.4	46.1	28900	0.13	489	34.8	39.3	155	1150	3.130
CS175	29200	1.020	52.4	39.7	26500	0.08	464	30.4	37.5	136	1080	2.532
CS175-B	23000	1.380	48.5	36.4	21600	0.24	359	30.8	46.8	131	931	2.246
CS176	33300	1.150	59.1	46.3	30000	0.15	592	35.4	39.0	156	1180	3.099
CS176-S	27500	1.100	48.7	41.5	26200	0.15	665	38.4	29.5	136	1110	3.229
CS177	28600	0.976	49.5	38.1	26000	0.12	495	30.8	32.8	132	1020	2.599
CS179	28200	1.020	50.6	38.9	26500	0.14	488	31.5	35.2	136	1090	2.227
CS-179-B	20400	1.070	41.5	30.0	20300	0.16	344	26.9	36.2	108	909	1.945
CS-179-S	23900	1.040	42.9	34.0	22900	0.12	445	33.7	26.5	120	956	3.079
CS181	25500	1.010	47.9	35.6	24300	0.13	435	29.9	33.2	126	996	2.030
CS-181-B	22900	1.290	47.7	35.9	22300	0.20	366	31.2	43.3	124	952	2.141
CS-181-S	21700	0.916	39.7	30.6	20800	0.13	386	28.4	27.0	110	698	2.528
CS182	24300	0.901	43.8	31.8	23500	0.12	492	28.4	27.2	117	1090	2.507
CS-182-S	23500	0.939	42.4	33.4	23000	0.12	513	32.3	26.3	116	986	2.827
Lowest Effect Level		0.6	26	16	2%	0.2	460	16	31	120	600	1
Severe Effect Level **		10	110	110	4%	2	1100	75	250	820	2000	10

**TABLE 3:** Particle size data for sediment samples (top 10 cm core sample) collected from the St. Lawrence River, 1997. (n=1)  
B - bottom 10 cm of the core. S - surface sample (top 3 cm).

Station Number	Percent Sand	Percent Silt	Percent Clay		Station Number	Percent Sand	Percent Silt	Percent Clay
CS105	15.7	52.4	31.9		CS167-S	36.7	45.4	17.9
CS109	14.2	55.9	29.9		CS167	27.9	51.6	20.5
CS109-S	9.0	68.6	22.4		CS167-B	8.7	60.6	30.6
CS115	17.6	60.9	21.5		CS168-S	45.0	38.7	16.2
CS115-S	33.0	42.8	24.1		CS168	42.1	42.1	15.9
CS117-S	42.2	35.2	22.5		CS168-B	3.7	62.4	34.0
CS117	51.2	33.3	15.5		CS171	35.2	43.6	21.1
CS126-S	55.6	28.4	16.0		CS172	9.9	59.4	30.6
CS126	58.3	30.5*	10.5*		CS173	5.4	66.0	28.6
CS127	68.6	18.2	13.2		CS175	12.9	59.1	28.0
CS128-S	65.8	18.8	15.4		CS175-B	13.7	64.8	21.5
CS128	39.8	42.3	16.8		CS176-S	3.6	61.8	34.6
CS131-S	25.9	52.6	21.5		CS176	6.2	65.0	28.8
CS131	35.7	43.1	21.2		CS177	13.5	58.4	28.2
CS132	39.0	38.0	23.0		CS179-S	11.4	59.1	29.5
CS135-S	38.6	39.5	21.8		CS179	14.2	57.7	28.1
CS135	33.2	44.9	21.9		CS179-B	22.1	55.0	22.9
CS156	48.6	31.7	19.7		CS181-S	11.8	60.1	28.1
CS164-S	16.5	60.0	23.5		CS181	11.5	62.2	26.3
CS164	29.0	53.6	17.4		CS181-B	16.2	59.6	24.2
CS166-S	9.3	66.4	24.3		CS182	14.0	56.1	29.9
CS166	7.6	66.2	26.2		CS182-S	9.8	57.1	33.1
CS166-B	6.1	65.4	28.5					

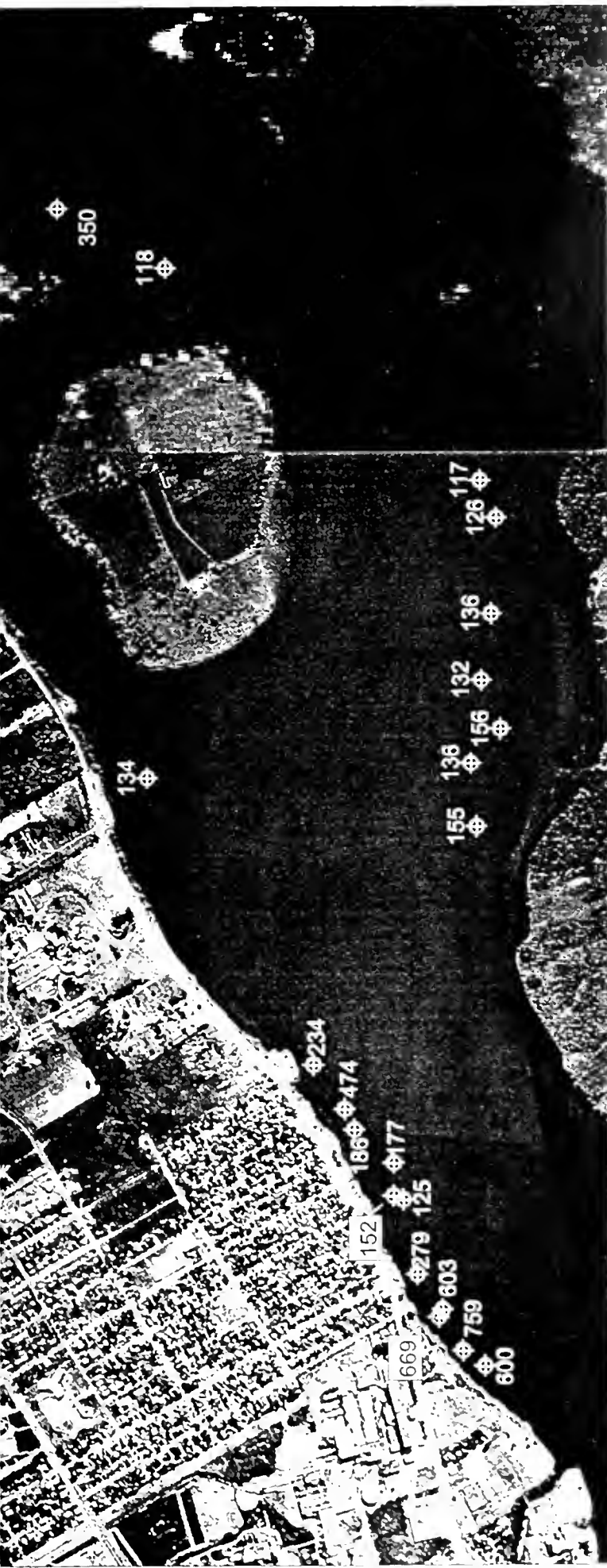
\* estimated value-lab reported 41% for silt+clay



Figure 2: Measured mercury concentrations (ppm) in sediment (top 10 cm).

**TABLE 4:** Median metal, total phosphorus and TOC concentrations ( $\mu\text{g/g}$  dry weight) in sediment samples (top 10 cm core sample and 3 cm surface samples) collected from the St. Lawrence River, 1997.

Parameters	Median, Minimum and Maximum Concentrations of Contaminants in Sediment											
	North Shore						South Shore					
	Surface (3 cm)	min	max	Core (10 cm)	min	max	Surface (3 cm)	min	max	Core (10 cm)	min	max
Aluminum	14800	10300	23400	16800	9630	31200	23700	21700	27500	28600	24300	33300
Cadmium	0.758	0.359	1.120	0.888	0.473	1.450	0.990	0.916	1.100	1.020	0.901	1.210
Chromium	32.0	25.1	49.1	37.5	23.8	58.8	42.7	39.7	48.7	50.6	43.8	59.1
Copper	37.6	19.3	57.6	42.5	16.9	60.9	33.7	30.6	41.5	38.9	31.8	46.3
Iron	15900	13100	22200	17300	12700	26600	22950	20800	26200	26500	23500	30000
Mercury	1.63	0.70	14.70	3.06	0.44	19.50	0.13	0.12	0.15	0.13	0.08	0.15
Manganese	293	222	357	292	201	439	479	386	665	489	435	592
Nickel	24.9	14.5	30.2	24.0	13.8	34.1	33.0	28.4	38.4	30.8	28.4	35.4
Total Phosphorus	852	653	1020	745	457	1150	971	698	1110	1090	996	1180
Lead	33.7	19.7	156.0	44.0	25.2	136.0	26.8	26.3	29.5	35.2	27.2	39.3
Zinc	133	69	673	186	102	759	118	110	136	136	117	156
TOC (%)	2.370	1.753	3.491	2.516	1.681	4.037	2.953	2.528	3.229	2.532	2.030	3.130



0.5 0 0.5 1 Kilometers

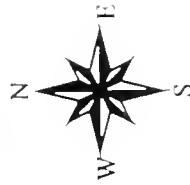


Figure 3: Measured zinc concentrations (ppm) in sediment ( top 10 cm).



The surface samples (3 cm) collected from both sides of the channel showed a similar pattern of sediment quality as discussed above for the 10 cm core samples.

The principal components analysis (PCA) was performed on log transformed data using surface samples (3 cm) and core samples (top 10 cm). The first axis grouped all variables together with the exception of lead, copper and zinc which all subsequently ranked high on the second axis (Table 5). Mercury was grouped on both the first and second axis however it was negatively correlated with the other parameters on the first axis and positively correlated with lead, copper and zinc on the second axis. The second axis was dominated by the variables associated with the former local discharge of contaminants from Courtaulds. These parameters were correlated with one another and stations with high concentrations of Hg, Zn, Cu, and Pb grouped together and were all located downstream, or in the vicinity of the Courtaulds shore based outfalls (Figure 4).

The stations on the south shore of the channel where concentrations of the parameters were low were also all grouped together in the lower right side of the graph. Figure 4 shows station 167 and 168 (downstream of the Domtar/ICI diffuser) grouped with stations that were high in Hg but with relatively low concentrations of Zn, Pb, and Cu. The first axis explained 59% of the variation in the data. By including the second axis 81% of the variability was explained.

The PCA using only percent silt produced results which were the same as the original analysis which used percent silt, clay and sand ensuring that the outcome of the first PCA was not artificially driven by overweighting the analysis with particle size variables (Appendix D). The PCA was again repeated using only data from the north shore and the results and overall conclusions were the same as described above. As well, the PCA using only core data also resulted in the same conclusions.

### **Particle Size Corrections of Sediment Contaminant Data**

A comparison of particle size corrected data from Cornwall with data from Maitland shows that the sediment downstream of the Cornwall point sources was not enriched with cadmium, chromium, iron, manganese and nickel. For these parameters, the ratios (metal:Al) generated for surface and core samples collected from both the north and south side of the channel were all less than the lower 95% confidence interval or were within the confidence bands generated for the Maitland data. When the data were corrected by normalizing metal concentrations at all stations to a fine particle (<63  $\mu\text{m}$ ) content of 74 % the results showed the same pattern. All data for the comparisons between the study area and reference area are provided in Appendix B(1), B(2) & B(3).

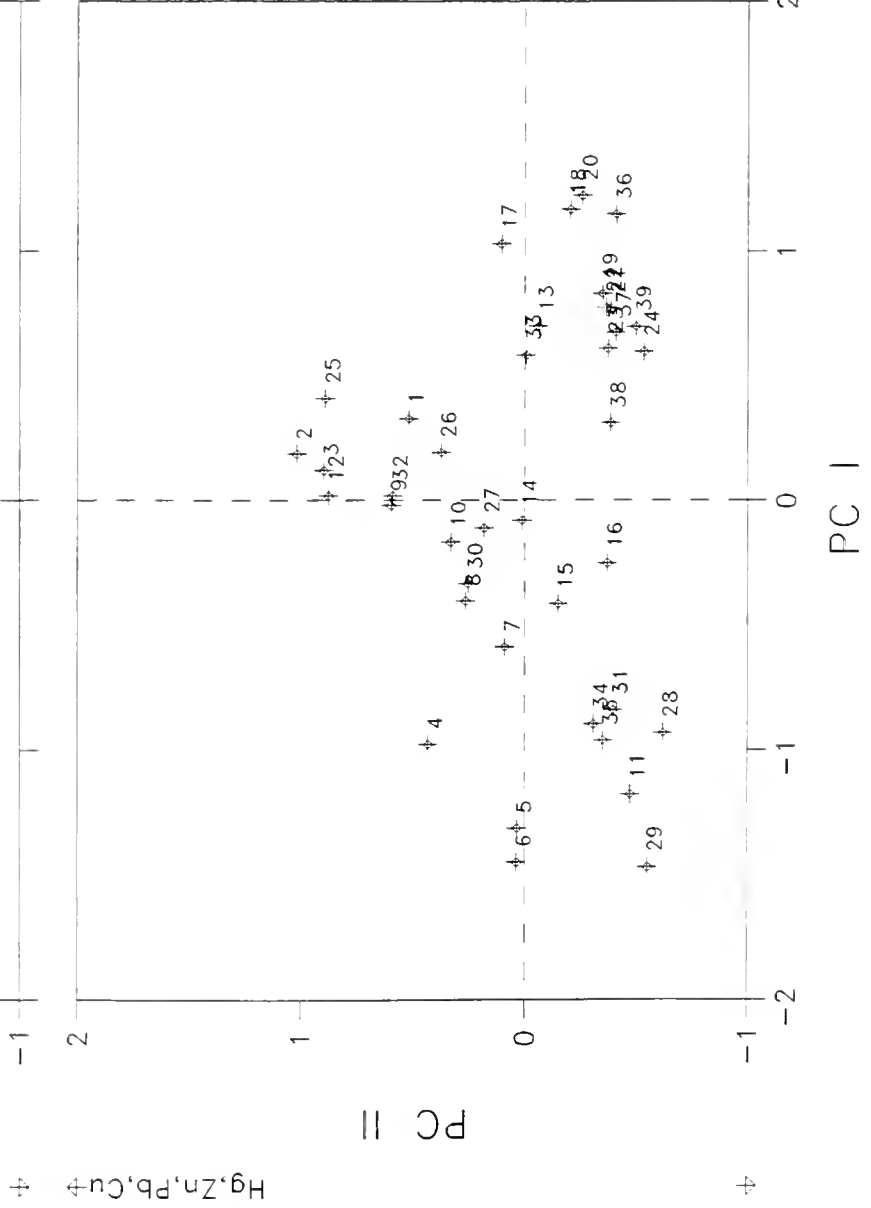
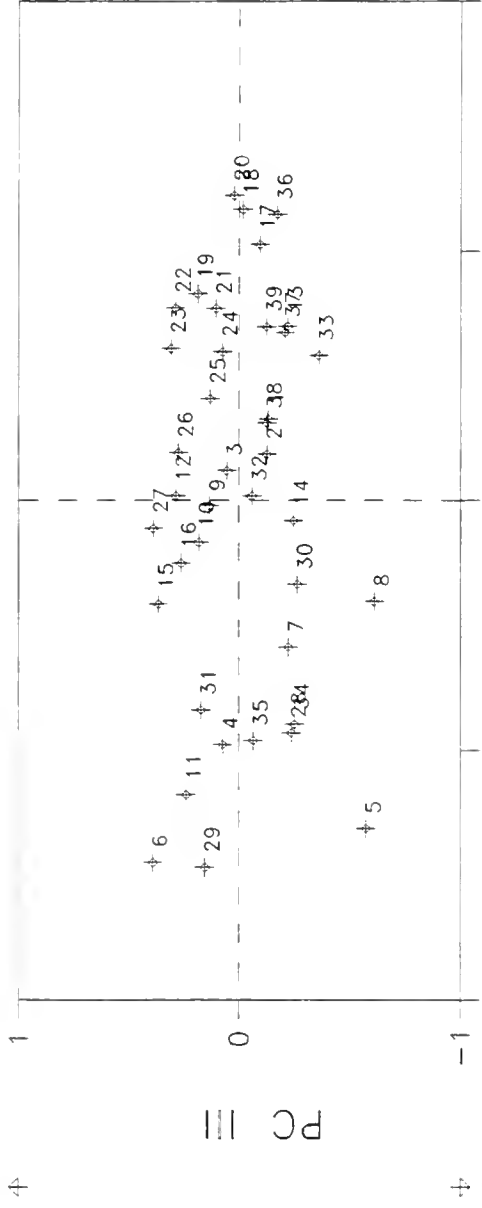
The copper, lead, mercury and zinc ratios for samples collected from the south side of the north channel were all less than the lower 95% confidence interval generated for the upstream reference area confirming previous observations that there was no enrichment of these parameters along the south shore. The corrected concentrations for these parameters calculated

**TABLE 5:** Component loadings and percent of total variance explained for the PCA of sediment quality in the St. Lawrence River, 1997.

Log Transformed Data			
	PC I	PC II	PC III
Aluminum	0.944	-0.141	0.1
Cadmium	0.842	0.3	-0.026
Chromium	0.948	0.19	0.175
Copper	0.621	0.721	0.044
Iron	0.904	-0.291	0.06
Mercury	-0.612	0.653	-0.207
Manganese	0.79	-0.431	0.104
Nickel	0.936	0.018	-0.028
Phosphorus	0.785	-0.295	0.23
Lead	0.135	0.922	0.271
Zinc	0.208	0.923	0.13
TOC	0.496	0.176	-0.8
Sand	-0.939	-0.058	0.136
Silt	0.891	0.12	-0.113
Clay	0.859	-0.11	-0.14
Percent of total variance explained			
	59%	81%	87%

Figure 4

Station Number	PCA Plot	Station Number	PCA Plot	Station Number	PCA Plot
CS-105	1	CS-175	19	CS-179s	37
CS-109	2	CS-176	20	CS-181s	38
CS-115	3	CS-177	21	CS-182s	39
CS-117	4	CS-179	22		
CS-126	5	CS-181	23		
CS-127	6	CS-182	24		
CS-128	7	CS-109s	25		
CS-131	8	CS-115s	26		
CS-132	9	CS-117s	27		
CS-135	10	CS-126s	28		
CS-156	11	CS-128s	29		
CS-164	12	CS-131s	30		
CS-166	13	CS-135s	31		
CS-167	14	CS-164s	32		
CS-168	15	CS-166s	33		
CS-171	16	CS-167s	34		
CS-172	17	CS-168s	35		
CS-173	18	CS-176s	36		



⊕ Sand, Hg

⊕ Al,Cd,Cr,Fe,Mn,Ni,Clay

⊕

⊕

by normalizing metal concentrations at all stations to a fine particle ( $<63\ \mu\text{m}$ ) content of 74 % provided the same conclusions supporting the results from the aluminum normalization method.

Core samples collected along the Cornwall waterfront at stations CS109, CS115, CS117 and CS164 had Cu:Al and Pb:Al ratios that were greater than the upper 95% confidence interval generated for Maitland indicating enrichment (Figure 5). For copper, this also occurred at station CS126 and CS132 and for lead this also occurred at station CS127. The results suggest enrichment of copper and lead at these stations. For surface samples (top 3 cm) stations CS109, CS115 and CS164 showed copper enrichment relative to Maitland while only station CS109 and CS164 showed lead enrichment. These stations were all located downstream of Courtaulds which has been associated with the discharge of these parameters.

All the core samples collected on the north shore had higher ratios of Zn:Al than the 95% upper confidence limit generated for the upstream reference area with the exception of stations CS166, CS167 and CS168 located downstream of the Domtar/ICI diffuser but upstream of Courtaulds. This is consistent with patterns of zinc discharge which was primarily from Courtaulds. Ratios of Zn:Al were approximately two to six times higher downstream of Courtaulds when compared to ratios generated for stations located upstream of the facility. The ratios calculated for the surface samples (3 cm) generally showed the same pattern.

Corrected concentrations of zinc and lead calculated by normalizing metal concentrations at all stations to a fine particle ( $<63\ \mu\text{m}$ ) content of 74% showed the same pattern of contamination as the aluminum normalizing approach, with only one exception (station CS132). This method did not suggest copper enrichment relative to the upstream reference area, although qualitatively stations along the north shore were enriched relative to the south shore using corrected and uncorrected data. This is effectively an artifact of the correction method since some sampling stations in Maitland were greater than 90% sand. When corrected to a fine particle size content of 74% the extrapolated copper concentrations become exceedingly large making it more difficult to show enrichment.

All samples (surface and 10 cm core samples) along the north shore had higher Hg:Al ratios than the 95% upper confidence limits generated for Maitland, suggesting enrichment of all stations downstream of Cornwall point sources. This is consistent with local mercury discharge patterns. Ratios for the core samples ranged from 2 to 133 times higher than the upper confidence limit for the Maitland area with most ratios greater than 20 times higher. For surface samples, the ratios of Hg:Al were 5 to 114 times higher in Cornwall than the 95% upper confidence limit generated for Maitland. The same results applied to the particle size correction method.

### **Contaminants in Core Top Samples Compared With Core Bottom Samples**

Metal, total phosphorus and TOC concentrations in the bottom of the core samples collected from the three stations downstream of Domtar/ICI and the three stations from the south shore deposit were compared with the 10 cm core top samples and 3 cm surface samples from the same

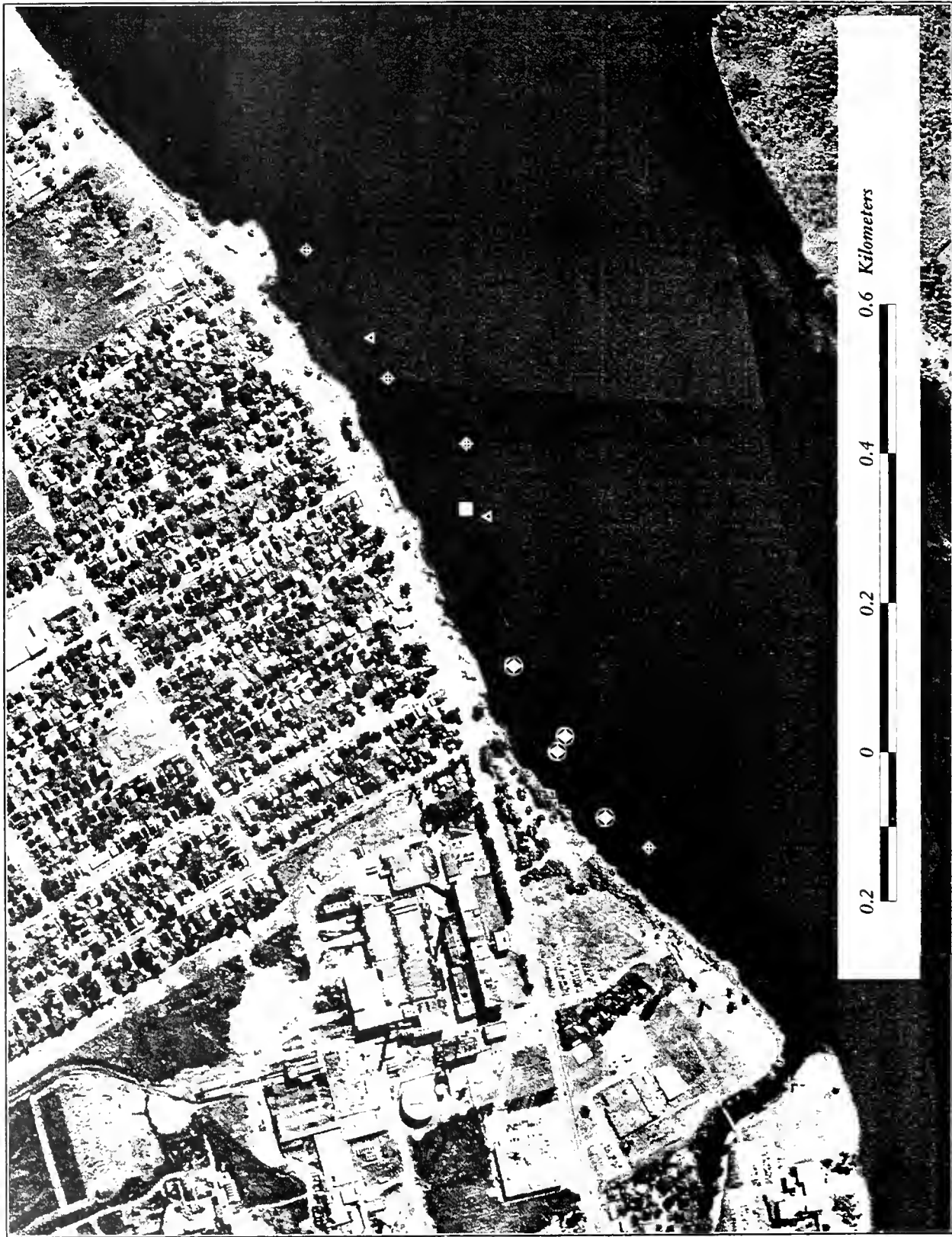


Figure 5: Local sediment enrichment of copper and lead.

locations to determine if there had been changes in sediment quality over time and to confirm whether these locations were historically contaminated with mercury. Concentrations of all parameters at station CS-166 (Downstream of Domtar/ICI) and at station CS175, CS179 and CS181 (south side deposit) in the bottom of the cores were similar to concentrations found in the top 10 cm core samples and surface samples for all metals, total phosphorus and TOC (Table 2). This suggests little change in sediment quality over time at these four stations based on the assumption that the samples collected from the bottom of the cores reflect historical conditions relative to the sediment located at the top of the cores. The particle size distribution (percent silt, clay and sand), in the top of the cores for these four stations was almost identical to the particle size distribution in samples collected from the bottom of the cores which strengthens the comparison of metal concentrations between the two sample types.

At station CS167 and CS168 (downstream of Domtar/ICI), sediment concentrations for many of the parameters were higher in the core bottom samples when compared with the 10 cm core top samples and 3 cm surface samples, however, this was likely due to differences in particle size distributions between the samples. The bottom of the cores were high in percentage clay plus silt (91.2% and 96.4% respectively) while the core top samples were much higher in percentage sand (Table 3). The percentage clay plus silt in the top of the cores was only 72.1% for station CS167 and 58% for CS168. The 3 cm surface samples at these two stations had similar metal concentrations as the 10 cm core top samples and similar particle size distributions (Table 2 & 3).

The metal concentrations in the samples from these two stations were corrected by normalizing the trace metals to aluminum concentrations. The ratios for all the parameters (with the exception of mercury), were similar between the core top samples and the core bottom samples verifying that the discrepancies in metal concentrations were likely due to particle size differences (Appendix B1).

However for mercury the correction method generated ratios that were three and five times higher in the bottom samples than the top samples respectively for station CS167 and CS168. This suggest that the high concentrations of mercury in the bottom samples at stations CS-167 and CS-168 were due to enrichment and cannot be due to particle size differences alone. These high concentrations most likely were due to upstream discharges of mercury from the Fly Creek sewer which historically discharged effluent from Domtar and ICI. Although station CS166 was close to stations CS167 and CS168 the data suggest it was not impacted by the upstream source since mercury concentrations were low in core top and bottom samples. More samples collected from this area would provide a better indication of the areal extent of impact by the upstream point source. Previous surveys show a patchy distribution in the area. However, these limited data support results from previous studies which showed that this area was contaminated. Historical data show that mercury concentrations were as high as 18.2  $\mu\text{g/g}$  in 1975 and 19.8  $\mu\text{g/g}$  in 1979 in the vicinity of the 1997 stations (MOE 1979; Kauss et al. 1988).

## Comparison of 1997 Data with 1994 Data

Split samples for interlaboratory comparisons between MOE and EC for metal and particle size analysis were compared using a paired t-test. The paired t-test showed there was no significant difference in trace metal data between the two laboratories for iron, chromium, mercury, manganese, nickel and lead ( $p > 0.05$ ). As well, there was no significant difference between the two laboratories for particle size analysis. The EC laboratory consistently reported higher aluminum values than the MOE lab ( $p < 0.001$ ), while the MOE lab reported higher cadmium ( $p < 0.001$ ), copper ( $p < 0.01$ ) and zinc ( $p < 0.02$ ) concentrations. Results of the statistical analysis are presented in Table 6 (raw data are provided in Appendix E). A comparison of sediment data between years to determine changes in sediment quality over time was therefore limited to parameters with concentrations that were not found to be significantly different between laboratories.

The effect of these results on the particle size correction methods and subsequent comparison of the sediment quality in the Cornwall area with the upstream reference area which had sediment that was analyzed by the MOE laboratory, actually underestimates the contamination in Cornwall. The identification of sites that were enriched with Hg, Zn, Cu and Pb was conservative using either method of particle size correction with both correction methods likely underestimating the number of sites that were enriched.

Since previous surveys suggest that the sediment quality in the study area was heterogeneous (MOE 1979; Richman 1996), direct comparison of data on a station by station basis between years required that the stations be located close to one another for the comparison to be relevant. The 1994 QA/QC data using triplicate core samples from six stations showed that within station variability increased when the distance between replicate cores increased from 1 to 7 meters. The 1997 QA/QC data (Appendix C) for within station variability showed good agreement in concentrations for samples collected about 7 meters apart but variability increased as distance between samples increased. Based on the northing and easting recorded in the field in 1997, stations CS105, CS109, CS117, CS127, CS135 and CS164 were not considered to be the same as their counterparts in the 1994 survey. The remaining stations were close ( $< 8$  meters) to the original stations in 1994 allowing for better data comparisons (northing and easting data provided in Appendix A).

Accordingly, results from the 1997 survey for stations CS115, CS126, CS128, CS131, CS132 and CS156 were compared with results from the same locations collected in 1994 using a paired t-test to determine if there was a change in sediment quality. Using 1994 and 1997 data corrected for particle size differences (by normalizing the contaminant concentrations to a particle content of 74% fines) there was no significant difference in sediment concentrations between 1994 and 1997 for mercury, chromium, nickel, iron and manganese. There was a statistical difference in concentrations between years for lead ( $p < 0.01$ ), phosphorus ( $p < 0.001$ ) and TOC ( $p < 0.01$ ) (Table 7).

**TABLE 6: Paired t-Test for a comparison between analytical results generated by the Ministry of Environment (MOE) and Environment Canada (EC).**  
Sediment samples collected from the St. Lawrence River, 1997 were split and analysed by the two laboratories.

Aluminum			Iron			Chromium		
Mean	MOE	EC	Mean	MOE	EC	Mean	MOE	EC
Variance	4788571.43	11365535.7	Variance	6785714.29	4985714.3	Variance	45.93	38.10
Observations	8	8	Observations	8	8	Observations	8	8
Pearson Correlation	0.868		Pearson Correlation	0.865		Pearson Correlation	0.776	
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	7		df	7		df	7	
t Stat	-9.768		t Stat	-0.540		t Stat	-1.813	
P(T<=t) one-tail	0.00001		P(T<=t) one-tail	0.303		P(T<=t) one-tail	0.056	
t Critical one-tail	1.895		t Critical one-tail	1.895		t Critical one-tail	1.895	
P(T<=t) two-tail	0.00002		P(T<=t) two-tail	0.606		P(T<=t) two-tail	0.113	
t Critical two-tail	2.365		t Critical two-tail	2.365		t Critical two-tail	2.365	

Cadmium			Mercury			Nickel		
Mean	MOE	EC	Mean	MOE	EC	Mean	MOE	EC
Variance	0.0427	0.0431	Variance	5.009	10.926	Variance	6.57	15.56
Observations	8	8	Observations	8	8	Observations	8	8
Pearson Correlation	0.842		Pearson Correlation	0.971		Pearson Correlation	0.696	
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	7		df	7		df	7	
t Stat	9.313		t Stat	-1.438		t Stat	-0.984	
P(T<=t) one-tail	0.00002		P(T<=t) one-tail	0.097		P(T<=t) one-tail	0.179	
t Critical one-tail	1.895		t Critical one-tail	1.895		t Critical one-tail	1.895	
P(T<=t) two-tail	0.00003		P(T<=t) two-tail	0.194		P(T<=t) two-tail	0.358	
t Critical two-tail	2.365		t Critical two-tail	2.365		t Critical two-tail	2.365	

Copper			Manganese			Lead		
Mean	MOE	EC	Mean	MOE	EC	Mean	MOE	EC
Variance	235.64	72.09	Variance	2678.57	1547.55	Variance	2257.14	1355.35
Observations	8	8	Observations	8	8	Observations	8	8
Pearson Correlation	0.988		Pearson Correlation	0.863		Pearson Correlation	0.995	
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
df	7		df	7		df	7	
t Stat	2.992		t Stat	-1.019		t Stat	1.892	
P(T<=t) one-tail	0.010		P(T<=t) one-tail	0.171		P(T<=t) one-tail	0.050	
t Critical one-tail	1.895		t Critical one-tail	1.895		t Critical one-tail	1.895	
P(T<=t) two-tail	0.020		P(T<=t) two-tail	0.342		P(T<=t) two-tail	0.100	
t Critical two-tail	2.365		t Critical two-tail	2.365		t Critical two-tail	2.365	

Table 6 continued

Zinc				Sand-Sum3			
	MOE	EC			MOE	EC	
Mean	323	267		Mean	35.6	33.6	
Variance	77535.71	48803.27		Variance	204.84	298.37	
Observations	8	8		Observations	8	8	
Pearson Correlation	0.997			Pearson Correlation	0.242		
Hypothesized Mean Difference	0			Hypothesized Mean Difference	0		
df	7			df	7		
t Stat	2.601			t Stat	0.298		
P(T<=t) one-tail	0.018			P(T<=t) one-tail	0.387		
t Critical one-tail	1.895			t Critical one-tail	1.895		
P(T<=t) two-tail	0.035			P(T<=t) two-tail	0.774		
t Critical two-tail	2.365			t Critical two-tail	2.365		

Clay -Sum1				Silt-Sum2			
	MOE	EC			MOE	EC	
Mean	17.0	18.7		Mean	47.1	47.6	
Variance	25.271	20.067		Variance	94.696	188.623	
Observations	8	8		Observations	8	8	
Pearson Correlation	0.489			Pearson Correlation	0.189		
Hypothesized Mean Difference	0			Hypothesized Mean Difference	0		
df	7			df	7		
t Stat	-1.003			t Stat	-0.081		
P(T<=t) one-tail	0.175			P(T<=t) one-tail	0.469		
t Critical one-tail	1.895			t Critical one-tail	1.895		
P(T<=t) two-tail	0.349			P(T<=t) two-tail	0.938		
t Critical two-tail	2.365			t Critical two-tail	2.365		

**TABLE 7:** Paired t-Test for a comparison between mean surface sediment concentrations (10 cm core samples) at selected stations in 1994 with concentrations measured in 1997. All data were corrected for particle size.

<i>Chromium</i>		1997	1994
Mean		41.8	43.6
Variance		35.58	40.13
Observations		6	6
Pearson Correlation		0.056	
Hypothesized Mean Difference		0	
df		5	
t Stat		-0.523	
P(T<=t) one-tail		0.312	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.624	
t Critical two-tail		2.571	

<i>Iron</i>		1997	1994
Mean		20501	20103
Variance		8711476.9	9008297.1
Observations		6	6
Pearson Correlation		-0.048	
Hypothesized Mean Difference		0	
df		5	
t Stat		0.227	
P(T<=t) one-tail		0.415	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.830	
t Critical two-tail		2.571	

<i>Mercury</i>		1997	1994
Mean		9.76	5.63
Variance		59.677	37.237
Observations		6	6
Pearson Correlation		0.746	
Hypothesized Mean Difference		0	
df		5	
t Stat		1.967	
P(T<=t) one-tail		0.053	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.106	
t Critical two-tail		2.571	

<i>Manganese</i>		1997	1994
Mean		373	334
Variance		3982.8	3056.4
Observations		6	6
Pearson Correlation		0.407	
Hypothesized Mean Difference		0	
df		5	
t Stat		1.475	
P(T<=t) one-tail		0.100	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.200	
t Critical two-tail		2.571	

<i>Nickel</i>		1997	1994
Mean		25.4	30.4
Variance		31.26	23.90
Observations		6	6
Pearson Correlation		-0.566	
Hypothesized Mean Difference		0	
df		5	
t Stat		-1.306	
P(T<=t) one-tail		0.124	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.249	
t Critical two-tail		2.571	

<i>Lead</i>		1997	1994
Mean		57.4	76.2
Variance		430.02	365.23
Observations		6	6
Pearson Correlation		0.816	
Hypothesized Mean Difference		0	
df		5	
t Stat		-3.792	
P(T<=t) one-tail		0.006	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.013	
t Critical two-tail		2.571	

<i>Total Phosphorus</i>		1997	1994
Mean		853	1475
Variance		27462.9	44483.3
Observations		6	6
Pearson Correlation		0.600	
Hypothesized Mean Difference		0	
df		5	
t Stat		-8.800	
P(T<=t) one-tail		0.0002	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.0003	
t Critical two-tail		2.571	

<i>TOC</i>		1997	1994
Mean		3.590	5.184
Variance		1.6704	0.4412
Observations		6	6
Pearson Correlation		0.626	
Hypothesized Mean Difference		0	
df		5	
t Stat		-3.835	
P(T<=t) one-tail		0.006	
t Critical one-tail		2.015	
P(T<=t) two-tail		0.012	
t Critical two-tail		2.571	

The change in concentration (delta) was also calculated on both particle size corrected and uncorrected data to compare concentrations between years at each station (Table 8). The most noteworthy changes include a decrease in concentrations of lead, phosphorus and % TOC at all six stations (with the exception of Pb at CS132). These decreases were statistically significant according to results from the paired t-test (Table 7). Nickel concentrations were lower in 1997 than 1994 at five stations but the decrease was not statistically significant. Additionally, Hg concentrations increased at four stations, decreased at station CS126 and generally remained the same at station CS156. However, these changes in concentration were also not statistically significant. A review of the QA/QC analysis (Appendix C2) indicates that the coefficient of variance for Hg within the box corer was high relative to the other parameters (range - 12% to 23%). This variability should be considered when comparing concentrations between years. As well, QA/QC data used to examine within station variability (Appendix C3) show a patchy distribution for total phosphorus making it difficult to distinguish changes in phosphorus concentrations over time from the inherent spatial variability in the sediment.

Any conclusions regarding changes in sediment quality between 1994 and 1997 for the study area based on this limited data set are tentative. It is unknown if three years between sampling dates is sufficient to measure real change in sediment contaminant concentrations in a river where sediment transport, deposition and resuspension on an annual basis may be significant.

### **Comparison of Surface Sample (3 cm) Concentrations With Concentrations in the Surface Core Samples (10 cm).**

Since the sediment surface is subjected to constant mixing due to changes in flow, deposition of new sediment and resuspension of existing surface sediment in addition to mixing from bioturbation, differences in sediment concentration between the sediment layers requires cautious interpretation. An ANCOVA using particle size as the covariate was performed on the log transformed data to distinguish a difference between contaminant concentrations in surface samples and core samples. A test for heterogeneity of slopes showed that there was no significant difference between slopes for all parameters for the two sample types with the exception of lead ( $p < 0.02$ ) (Table 9). As a result lead was dropped from the analysis. Particle size accounted for a significant amount of the variation in sediment concentration for all parameters with the exception of zinc and total phosphorus.

The ANCOVA found that there was no significant difference in metal concentrations in the surface samples compared with the 10 cm core top samples for all the parameters tested with the exception of cadmium ( $p < 0.042$ ) and chromium ( $p < 0.036$ ) which showed weak statistical differences (Table 9). A Bonferroni correction to adjust the P value for multiple comparisons would likely find that these two parameters were not significantly different. This suggests that sediment quality has not changed at the surface relative to the underlying sediment for most parameters, however, sediment mixing due to bioturbation and other physical processes within the river may make any changes in sediment quality too small to measure.

**TABLE 8:** Surface sediment contaminant concentrations ( $\mu\text{g/g}$ ) (10 cm core data) from stations sampled in 1994 and 1997 and the change (Delta) in concentration between years. A negative Delta indicates that the concentration has increased from 1994 to 1997.

Station number 1994 / 1997	Chromium 1994	Chromium 1997	Delta Cr	Iron 1994	Iron 1997	Delta Fe	Mercury 1994	Mercury 1997	Delta Hg	Manganese 1994	Manganese 1997	Delta Mn
CS15 / CS115	46.7	41.8	4.9	19000	16400	2600	1.55	3.66	-2.11	300	281	19
CS26 / CS126	29.1	23.8	5.3	15061	12700	2361	10.94	5.20	5.74	257.98	201	57
CS28 / CS128	35.1	32.7	2.4	17116	17900	-784	3.86	11.20	-7.34	321.47	345	-24
CS31 / CS131	36.0	33.3	2.7	16000	18300	-2300	12.25	19.50	-7.25	260.00	347	-87
CS32 / CS132	40.0	43.8	-3.8	16269	17300	-1031	ND	6.78	-6.78	250.84	329	-78
CS56 / CS156	27.0	26.2	0.8	14000	14400	-400	0.61	0.80	-0.19	230.00	272	-42
CS31 / CS131 (3 cm grab)	31.7	32.0	-0.3	14528	14700	-172	2.07	14.70	-12.63	240.88	288	-47
1994 / 1997	Nickel 1994	Nickel 1997	Delta Ni	Lead 1994	Lead 1997	Delta Pb	Phosphorus 1994	Phosphorus 1997	Delta TP	%TOC 1994	%TOC 1997	Delta TOC
CS15 / CS115	27.7	26.6	1.1	113.3	99.8	13.5	1170	678	492	4.01	2.45	1.6
CS26 / CS126	21.3	19.1	2.2	59.5	25.2	34.3	1170	457	713	5.00	3.07	1.9
CS28 / CS128	25.5	18.0	7.5	57.4	37.3	20.1	1400	681	719	5.00	2.85	2.2
CS31 / CS131	25.0	17.8	7.2	58.0	40.6	17.4	1360	659	701	4.64	4.04	0.6
CS32 / CS132	26.5	24.6	1.9	59.2	63.3	-4.1	1150	818	332	4.02	2.52	1.5
CS56 / CS156	21.0	14.6	6.4	37.0	26.7	10.3	930	745	185	2.83	1.74	1.1
CS31 / CS131 (3 cm grab)	20.8	24.9	-4.1	40.2	33.7	6.5	1080	853	227	3.09	2.74	0.4

Data Corrected for Particle Size - Sediment contaminant data were normalized to a fine ( $< 63 \mu\text{m}$ ) particle content of 74% .

Station number 1994 / 1997	Chromium 1994	Chromium 1997	Delta Cr	Iron 1994	Iron 1997	Delta Fe	Mercury 1994	Mercury 1997	Delta Hg	Manganese 1994	Manganese 1997	Delta Mn
CS15 / CS115	47.4	37.6	9.8	19286	14748	4538	1.57	3.29	-1.72	305	253	52
CS26 / CS126	32.6	43.0	-10.5	16828	22953	-6125	12.22	9.40	2.83	288	363	-75
CS28 / CS128	42.1	41.0	1.1	20556	22443	-1887	4.64	14.04	-9.41	386	433	-46
CS31 / CS131	41.7	38.4	3.3	18539	21089	-2550	14.19	22.47	-8.28	301	400	-99
CS32 / CS132	48.5	53.2	-4.7	19747	21015	-1269	ND	8.24	-8.24	304	400	-95
CS56 / CS156	49.5	37.8	11.7	25659	20760	4900	1.12	1.15	-0.03	422	392	29
CS31 / CS131 (3 cm grab)	47.7	32.0	15.7	21858	14700	7158	3.11	14.70	-11.59	362	288	74
1994 / 1997	Nickel 1994	Nickel 1997	Delta Ni	Lead 1994	Lead 1997	Delta Pb	Phosphorus 1994	Phosphorus 1997	Delta TP	%TOC 1994	%TOC 1997	Delta TOC
CS15 / CS115	28.1	23.9	4.2	115.0	89.7	25.3	1188	610	578	4.07	2.20	1.87
CS26 / CS126	23.8	34.5	-10.7	66.5	45.5	21.0	1307	826	481	5.59	5.55	0.04
CS28 / CS128	30.6	22.6	8.0	68.9	46.8	22.1	1681	854	828	6.00	3.57	2.43
CS31 / CS131	29.0	20.5	8.5	67.2	46.8	20.4	1576	759	816	5.38	4.65	0.72
CS32 / CS132	32.2	29.9	2.3	71.8	76.9	-5.1	1396	994	402	4.88	3.06	1.82
CS56 / CS156	38.5	21.0	17.4	67.8	38.5	29.3	1705	1074	630	5.19	2.51	2.68
CS31 / CS131 (3 cm grab)	31.3	24.9	6.4	60.5	33.7	26.8	1625	853	772	4.65	2.74	1.91

ND - not detected

**TABLE 9:** Results of the analysis of covariance for each term included in the general linear model testing for sample type (10 cm core samples vs 3 cm surface samples) variability. The data is reported for each parameter measured in sediment from the St. Lawrence River, 1997.

Contaminant		F-ratio	P	Contaminant		F-ratio	P
Aluminum	Particle size	64.57	0.0001	Manganese	Particle size	16.91	0.0003
	Sample type	1.39	0.249		Sample type	0.11	0.7479
	Particle size *sample type	0.68	0.4169		Particle size *sample type	0.75	0.3953
Cadmium	Particle size	50.95	0.0001	Nickel	Particle size	81.46	0.0001
	Sample type	4.58	0.0418		Sample type	0.01	0.9307
	Particle size *sample type	0	0.9703		Particle size *sample type	0.51	0.4804
Chromium	Particle size	72.88	0.0001	Lead	Particle size	20.25	0.0001
	Sample type	4.87	0.0364		Sample type	1.81	0.1896
	Particle size *sample type	0.75	0.3934		Particle size *sample type	6.76	0.0152
Copper	Particle size	13.53	0.0011	Zinc	Particle size	1.22	0.2799
	Sample type	3.96	0.0572		Sample type	1.86	0.1848
	Particle size *sample type	0.73	0.401		Particle size *sample type	0.5	0.4876
Iron	Particle size	30.08	0.0001	Total Phosphorus	Particle size	1.87	0.1831
	Sample type	0.42	0.5208		Sample type	1.09	0.3063
	Particle size *sample type	2.1	0.1591		Particle size *sample type	0.6	0.4446
Mercury	Particle size	5.5	0.0269	Total Organic Carbon	Particle size	4.41	0.0456
	Sample type	1.14	0.2954		Sample type	0.12	0.7357
	Particle size *sample type	1.91	0.1784		Particle size *sample type	2.92	0.0991

## CONCLUSIONS

The following conclusions have been based on the stated survey objectives.

1) *Surface sediment located in the deposition zone about 1.4 km downstream of the Domtar/ICI diffuser has mercury concentrations greater than the LEL but less than the SEL.*

*Sediment at this site was historically contaminated with mercury. This is evident from high concentrations in sediment collected from the bottom of the core (4.63 ug/g and 13.70 ug/g) relative to mercury concentrations in sediment at the top of the core sample (1.19 ug/g and 1.71 ug/g respectively) .*

*This area was not contaminated with other metals.*

2) *Sediment located adjacent to the north east side of Cornwall Island was not contaminated with metals.*

3) *The highest concentrations of mercury, lead, copper and zinc in the study area were located downstream of the former Courtaulds Fibre Canada facility. Remediation of contaminated sediment, if considered, should be focussed in this deposition zone. Sampling sites in this area could be used for future monitoring to assess temporal changes in sediment quality.*

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## APPENDIX



**APPENDIX A:** Station location for sediment sampling survey in the St. Lawrence River, 1997.

Station	Sampling Date	Northing	Easting	1994 station locations	Northing	Easting
CS105	97-10-22	4984819.60	523938.0	CS05	4984856.3	523925.8
CS109	97-10-22	4984878.70	523978.8	CS09	4984887.7	523966.0
CS115	97-10-22	4984932.70	524087.5	CS15	4984933.8	524079.1
CS117	97-10-22	4985001.00	524182.0	CS17	4984991.1	524180.5
CS126	97-10-23	4985038.20	524381.7	CS26	4985031.2	524382.7
CS127	97-10-22	4985064.40	524391.8	CS27	4985076.7	524403.7
CS128	97-10-23	4985063.90	524479.0	CS28	4985061.0	524478.3
CS131	97-10-23	4985169.20	524567.2	CS31	4985167.6	524564.7
CS132	97-10-23	4985195.00	524621.7	CS32	4985190.8	524620.1
CS135	97-10-23	4985277.50	524738.5	CS35	4985276.6	524722.7
CS156	97-10-21	4985718.00	525505.1	CS56	4985722.6	525503.0
CS164	97-10-22	4984943.30	524067.5	CS64	4984953.3	524056.6
CS166	97-10-21	4984027.00	521105.6	CS31-S	4985172.5	524564.1
CS167	97-10-22	4984039.00	521149.9			
CS168	97-10-21	4984060.60	521183.4			
CS171	97-10-21	4985668.00	526865.0			
CS172	97-10-21	4985955.70	527025.8			
CS173	97-10-23	4984838.00	525372.6			
CS175	97-10-23	4984852.30	525541.7			
CS176	97-10-23	4984773.90	525632.6			
CS177	97-10-23	4984825.00	525763.0			
CS179	97-10-23	4984798.60	525940.0			
CS181	97-10-21	4984785.00	526195.0			
CS182	97-10-21	4984827.90	526295.7			

QA/QC site locations

CS126	97-10-23	4985031.5	524387.2	
CS164	97-10-22	4984945.7	524067.9	
CS167	97-10-22	4984040.5	521143.4	
CS176	97-10-23	4984776.7	525619.3	Samples not submitted
CS135	97-10-23	Data unavailable		

Estimated Core Lengths

CS166	29 cm
CS167	20 cm
CS168	23 cm
CS175	24 cm
CS179	20 cm
CS181	24 cm

**APPENDIX B(1):** Particle size correction. Sediment contaminant data (10 cm surface core samples) were normalized to aluminum concentrations.  
 St. Lawrence River, 1997. B - bottom 10 cm of the core. S - surface sample (top 3 cm).

Station Number	Cd:Al	Cr:Al	Cu:Al	Fe:Al	Hg:Al	Mn:Al	Ni:Al	P:Al	Pb:Al	Zn:Al	TOC:Al
CS105	0.000049	0.002388	0.002301	0.984694	0.000085	0.015051	0.001367	0.038827	0.003230	0.030612	1.492857
CS109	0.000071	0.002667	0.003358	1.006061	0.000293	0.015273	0.001588	0.038667	0.008242	0.046000	1.740606
CS115	0.000094	0.002714	0.003760	1.064935	0.000238	0.018247	0.001727	0.044026	0.006481	0.039156	1.588312
CS117	0.000053	0.002730	0.003035	1.156522	0.000174	0.021304	0.001730	0.047739	0.007261	0.024261	2.046087
CS126	0.000075	0.002471	0.002762	1.318795	0.000540	0.020872	0.001983	0.047456	0.002617	0.012980	3.194185
CS127	0.000035	0.002059	0.002178	1.007407	0.000320	0.020741	0.001022	0.040593	0.003970	0.011259	1.245185
CS128	0.000038	0.001946	0.002000	1.065476	0.000667	0.020536	0.001071	0.040536	0.002220	0.010536	1.696429
CS131	0.000038	0.001959	0.002500	1.076471	0.001147	0.020412	0.001047	0.038765	0.002388	0.010941	2.374706
CS132	0.000044	0.002009	0.002794	0.793578	0.000311	0.015092	0.001128	0.037523	0.002904	0.021743	1.154128
CS135	0.000052	0.002121	0.002395	0.973684	0.000197	0.017421	0.001205	0.034737	0.003095	0.012316	1.109474
CS156	0.000043	0.002298	0.001482	1.263158	0.000070	0.023860	0.001281	0.065351	0.002342	0.011754	1.526316
CS164	0.000056	0.003044	0.003744	1.106250	0.000191	0.018250	0.001556	0.052938	0.008500	0.041813	1.533750
CS166	0.000050	0.001947	0.001770	0.942623	0.000033	0.014754	0.001127	0.047131	0.001475	0.005410	1.326230
CS167	0.000054	0.002202	0.002363	0.970238	0.000071	0.015774	0.001780	0.051607	0.002179	0.006369	1.767857
CS168	0.000052	0.002206	0.001865	1.000000	0.000101	0.017059	0.001412	0.055706	0.002235	0.006000	1.066471
CS171	0.000037	0.001962	0.001683	1.026882	0.000023	0.019301	0.001108	0.049355	0.001591	0.006344	1.083871
CS172	0.000036	0.001885	0.001478	0.852564	0.000020	0.014071	0.001093	0.035897	0.001410	0.011218	1.070513
CS173	0.000037	0.001786	0.001410	0.883792	0.000004	0.014954	0.001064	0.035168	0.001202	0.004740	0.957187
CS175	0.000035	0.001795	0.001360	0.907534	0.000003	0.015890	0.001041	0.036986	0.001284	0.004658	0.867123
CS176	0.000035	0.001775	0.001390	0.900901	0.000005	0.017778	0.001063	0.035435	0.001171	0.004685	0.930631
CS177	0.000034	0.001731	0.001332	0.909091	0.000004	0.017308	0.001077	0.035664	0.001147	0.004615	0.908741
CS179	0.000036	0.001794	0.001379	0.939716	0.000005	0.017305	0.001117	0.038652	0.001248	0.004823	0.789716
CS181	0.000040	0.001878	0.001396	0.952941	0.000005	0.017059	0.001173	0.039059	0.001302	0.004941	0.796078
CS182	0.000037	0.001802	0.001309	0.967078	0.000005	0.020247	0.001169	0.044856	0.001119	0.004815	1.031687
CS-166-B	0.000048	0.001967	0.001707	0.870370	0.000005	0.012148	0.001215	0.042222	0.001637	0.005259	1.208519
CS-167-B	0.000057	0.001781	0.002607	0.607287	0.000187	0.010000	0.001571	0.045344	0.002360	0.006397	2.730769
CS-168-B	0.000062	0.002012	0.002934	0.664063	0.000535	0.011172	0.001402	0.042578	0.002875	0.007305	2.272656
CS-175-B	0.000060	0.002109	0.001583	0.939130	0.000011	0.015609	0.001339	0.040478	0.002035	0.005696	0.976522
CS-179-B	0.000052	0.002034	0.001471	0.995098	0.000008	0.016863	0.001319	0.044559	0.001775	0.005294	0.953431

Station Number	Cd:Al	Cr:Al	Cu:Al	Fe:Al	Hg:Al	Mn:Al	Ni:Al	P:Al	Pb:Al	Zn:Al	TOC:Al
CS-181-B	0.000056	0.002083	0.001568	0.973799	0.000009	0.015983	0.001362	0.041572	0.001891	0.005415	0.934934
CS-109-S	0.000049	0.002584	0.002926	0.978947	0.000305	0.016684	0.001374	0.053684	0.008211	0.035421	1.448947
CS-115-S	0.000056	0.002253	0.002969	1.000000	0.000084	0.017474	0.001443	0.050361	0.003119	0.017268	1.168041
CS-117-S	0.000046	0.002171	0.002289	0.994652	0.000072	0.017807	0.001380	0.051604	0.003251	0.014439	1.095722
CS-126-S	0.000035	0.002336	0.001787	1.540984	0.000098	0.029262	0.001311	0.069836	0.001615	0.006721	2.442623
CS-128-S	0.000035	0.002437	0.002049	1.475728	0.000334	0.028447	0.001408	0.074272	0.002291	0.006699	1.845631
CS-131-S	0.000051	0.002148	0.002523	0.986577	0.000987	0.019329	0.001671	0.057248	0.002262	0.016846	1.836913
CS-135-S	0.000051	0.002211	0.001569	1.162602	0.000099	0.023415	0.001715	0.061626	0.002211	0.009512	1.425203
CS-164-S	0.000054	0.002595	0.003196	1.074324	0.000134	0.019662	0.001703	0.056824	0.006757	0.026689	1.906757
CS-166-S	0.000048	0.001936	0.001855	0.948718	0.000045	0.014316	0.001291	0.042137	0.001440	0.005684	1.491880
CS-167-S	0.000056	0.002189	0.001934	1.122951	0.000141	0.019590	0.001598	0.053525	0.001795	0.006303	1.942623
CS-168-S	0.000064	0.002271	0.001797	1.110169	0.000059	0.018814	0.001763	0.061356	0.002093	0.006839	1.845763
CS-176-S	0.000040	0.001771	0.001509	0.952727	0.000005	0.024182	0.001396	0.040364	0.001073	0.004945	1.174182
CS-179-S	0.000044	0.001795	0.001423	0.958159	0.000005	0.018619	0.001410	0.040000	0.001109	0.005021	1.288285
CS-181-S	0.000042	0.001829	0.001410	0.958525	0.000006	0.017788	0.001309	0.032166	0.001244	0.005069	1.164977
CS-182-S	0.000040	0.001804	0.001421	0.978723	0.000005	0.021830	0.001374	0.041957	0.001119	0.004936	1.202979

**APPENDIX B(2):** Particle size correction. Sediment contaminant data (10 cm surface core samples) were normalized to a fine (< 63  $\mu$ m) particle content of 74%. St. Lawrence River, 1997. B - bottom 10 cm of the core. S - surface sample (top 3 cm).

Station	Al Corrected mg/Kg	Cd Corrected mg/Kg	Cr Corrected mg/Kg	Cu Corrected mg/Kg	Fe Corrected mg/Kg	Hg Corrected mg/Kg	Mn Corrected mg/Kg	Ni Corrected mg/Kg	Pb Corrected mg/Kg	Zn Corrected mg/Kg	TP Corrected mg/Kg	TOC Corrected %
CS105	17228	0.837	41.1	39.6	16965	1.47	259	23.6	55.6	527	669	2.57
CS109	14250	1.010	38.0	47.8	14336	4.17	218	22.6	117.5	656	551	2.48
CS115	13849	1.304	37.6	52.1	14748	3.29	253	23.9	89.7	542	610	2.20
CS117	17462	0.923	47.7	53.0	20195	3.04	372	30.2	126.8	424	834	3.57
CS126	17404	1.301	43.0	48.1	22953	9.40	363	34.5	45.5	226	826	5.56
CS127	31858	1.116	65.6	69.4	32094	10.19	661	32.6	126.5	359	1293	3.97
CS128	21064	0.799	41.0	42.1	22443	14.04	433	22.6	46.8	222	854	3.57
CS131	19591	0.743	38.4	49.0	21089	22.47	400	20.5	46.8	214	759	4.65
CS132	26482	1.153	53.2	74.0	21015	8.24	400	29.9	76.9	576	994	3.06
CS135	21076	1.092	44.7	50.5	20522	4.16	367	25.4	65.2	260	732	2.34
CS156	16435	0.706	37.8	24.4	20760	1.15	392	21.0	38.5	193	1074	2.51
CS164	16699	0.927	50.8	62.5	18473	3.19	305	26.0	141.9	698	884	2.56
CS166	19568	0.978	38.1	34.6	18445	0.64	289	22.1	28.9	106	922	2.60
CS167	17266	0.935	38.0	40.8	16752	1.22	272	30.7	37.6	110	891	3.05
CS168	21719	1.120	47.9	40.5	21719	2.18	371	30.7	48.5	130	1210	2.32
CS171	21302	0.790	41.8	35.8	21875	0.50	411	23.6	33.9	135	1051	2.31
CS172	25688	0.922	48.4	38.0	21901	0.51	361	28.1	36.2	288	922	2.75
CS173	25614	0.948	45.7	36.1	22637	0.10	383	27.3	30.8	121	901	2.45
CS175	24842	0.868	44.6	33.8	22545	0.07	395	25.9	31.9	116	919	2.15
CS176	26306	0.908	46.7	36.6	23699	0.12	468	28.0	30.8	123	932	2.45
CS177	24472	0.835	42.4	32.6	22247	0.10	424	26.4	28.1	113	873	2.22
CS179	24355	0.881	43.7	33.6	22886	0.12	421	27.2	30.4	117	941	1.92
CS181	21351	0.846	40.1	29.8	20346	0.11	364	25.0	27.8	105	834	1.70
CS182	20938	0.776	37.7	27.4	20248	0.10	424	24.5	23.4	101	939	2.16
CS109-S	15471	0.756	40.0	45.3	15146	4.71	258	21.3	127.0	548	831	2.24
CS115-S	21488	1.196	48.4	63.8	21488	1.81	375	31.0	67.0	371	1082	2.51
CS117-S	24015	1.116	52.1	55.0	23887	1.73	428	33.1	78.1	347	1239	2.63
CS126-S	20361	0.708	47.6	36.4	31376	2.00	596	26.7	32.9	137	1422	4.97
CS128-S	22317	0.778	54.4	45.7	32933	7.45	635	31.4	51.1	150	1658	4.12
CS131-S	14900	0.758	32.0	37.6	14700	14.70	288	24.9	33.7	251	853	2.74
CS135-S	14868	0.754	32.9	23.3	17286	1.47	348	25.5	32.9	141	916	2.12
CS164-S	13134	0.706	34.1	42.0	14110	1.76	258	22.4	88.7	351	746	2.50
CS166-S	19117	0.915	37.0	35.5	18137	0.87	274	24.7	27.5	109	806	2.85
CS167-S	14282	0.804	31.3	27.6	16037	2.01	280	22.8	25.6	90	764	2.77

Station	Al Corrected mg/Kg	Cd Corrected mg/Kg	Cr Corrected mg/Kg	Cu Corrected mg/Kg	Fe Corrected mg/Kg	Hg Corrected mg/Kg	Mn Corrected mg/Kg	Ni Corrected mg/Kg	Pb Corrected mg/Kg	Zn Corrected mg/Kg	TP Corrected mg/Kg	TOC Corrected %
CS168-S	15927	1.018	36.2	28.6	17681	0.94	300	28.1	33.3	109	977	2.94
CS176-S	21138	0.846	37.4	31.9	20139	0.12	511	29.5	22.7	105	853	2.48
CS179-S	19989	0.870	35.9	28.4	19152	0.10	372	28.2	22.2	100	800	2.58
CS181-S	18231	0.770	33.4	25.7	17475	0.11	324	23.9	22.7	92	586	2.12
CS182-S	19305	0.771	34.8	27.4	18895	0.10	421	26.5	21.6	95	810	2.32
CS166-B	21307	1.018	41.9	36.4	18545	0.10	259	25.9	34.9	112	900	2.57
CS167-B	20069	1.154	35.8	52.3	12188	3.76	201	31.5	47.4	128	910	5.48
CS168-B	19678	1.222	39.6	57.7	13067	10.53	220	27.6	56.6	144	838	4.47
CS175-B	19749	1.185	41.6	31.3	18546	0.21	308	26.4	40.2	112	799	1.93
CS179-B	19405	1.018	39.5	28.5	19310	0.16	327	25.6	34.4	103	865	1.85
CS181-B	20249	1.141	42.2	31.7	19719	0.18	324	27.6	38.3	110	842	1.89

**APPENDIX B(3I):** Particle size correction. Sediment contaminant data were normalized to aluminum concentrations. Sediment samples were collected from the St. Lawrence River in 1991 at Maitland, Ontario. The mean, standard deviation and 95% upper and lower confidence intervals (CI) were generated from all the survey data from the study area. Maitland (n=116).

Maitland Data

	Cd Al	Cr Al	Cu Al	Fe Al	Hg Al	Mn Al	Ni Al	Pb Al	Zn Al	TP Al	TOC Al
Mean	7 842E-05	2 765E-03	2 484E-03	1 914E+00	7 485E-06	4 947E-02	1 977E-03	2 883E-03	7 308E-03	1 335E-04	1 340E-01
Standard Deviation	5 567E-05	4 651E-04	1 264E-03	7 845E-01	6 449E-06	2 029E-02	3 647E-04	3 619E-03	2 401E-03	6 658E-05	6 739E-02
95% upper CI	8 855E-05	2 849E-03	2 714E-03	2 057E+00	8 658E-06	5 316E-02	2 043E-03	3 542E-03	7 744E-03	1 456E-04	1 462E-01
95% lower CI	6 829E-05	2 680E-03	2 254E-03	1 772E+00	6 311E-06	4 578E-02	1 911E-03	2 225E-03	6 871E-03	1 214E-04	1 217E-01

**APPENDIX B(3II):** Particle size correction. Sediment contaminant data were normalized to a fine (< 63  $\mu$ m) particle content of 74%. Sediment samples collected from the St. Lawrence River in 1991 at Maitland, Ontario. The mean, standard deviation and 95% upper and lower confidence intervals (CI) were generated from all the survey data from the study area (ug/g dry weight). Maitland (n=116).

Maitland Data

	Cd Corrected	Cr Corrected	Cu Corrected	Fe Corrected	Hg Corrected	Mn Corrected	Ni Corrected	Pb Corrected	Zn Corrected	TP Corrected	TOC Corrected (%)	Al Corrected
Mean	2 17	85 67	67 01	62188	0 23	1562	59	83	211	4742	48	30906
Standard Deviation	2 12	64 16	36 60	52278	0 32	1135	34	122	124	6210	6 3	22222
95% upper CI	2 55	97 35	73 67	71701	0 29	1768	65	106	233	5873	5 9	34950
95% lower CI	1 78	73 99	60 35	52674	0 17	1355	52	61	188	3612	3 6	26862

Data from Richman and Townsend 1997

## APPENDIX C

### Quality Analysis\Quality Control - Among and Within-Station Variability.

Variability in sediment contaminant concentrations for all parameters among and within stations was compared using field replicates for core samples collected from four stations (CS126, CS135, CS164, CS167). Three replicate core samples were collected from within a single mini-box corer at each of the four stations. These results were used to assess among station variability and the variability associated within the mini-box corer. At each of the QA/QC stations a routine sample was also collected for the analyses described throughout this report. This sample which was collected from a separate drop of the mini-box corer was compared with the QA/QC samples from the same station to assess within station variability. Within sample variability was assessed by collecting split samples from one station (CS135). The three way split of each of two core samples from station CS135 was used to assess the variability associated with sample homogenization, possible sample contamination from handling practices, and laboratory "analytical error". Data for within sample variability was available for all parameters with the exception of mercury. All raw data are provided in Appendix C4.

An analysis of variance (ANOVA) was performed on both log transformed and non-transformed core data to estimate the proportion of the total variability associated with the between station and within mini-box core components (Appendix C1). The percent variability associated with each category was calculated by first calculating the variance components using the expected mean squares for each category and then comparing the variance components with the total variance.

Using the non-transformed data, the lowest source of variability in the core samples was associated with the within mini-box component for all parameters (with the exception of iron, manganese and total phosphorus). The percent variability associated with the two components were similar for chromium. This suggests that sediment within the confines of the mini-box corer was homogeneous for most parameters. The ANOVA found a significant difference between station concentrations (p values ranged from 0.0001 to 0.04) for all parameters tested with the exception iron, manganese and total phosphorus. Accordingly, for all parameters with the exception of iron, manganese and total phosphorus, the total variability within the mini-box corer was low enough that differences between stations could be determined.

The results of the ANOVA suggest that for iron, manganese and total phosphorus (chromium to a lesser extent), the variability in sediment concentrations within the box was greater than between stations. However, these results were likely due to the narrow range in concentrations for these parameters throughout the study area rather than due to large differences within the mini-box corer. Differences in concentrations between stations were not identified because the concentrations of these parameters in the sediment were similar among the stations.

The ANOVA using log transformed data provided the same results as described above.

For most parameters, variability (expressed as the coefficient of variance - CV Appendix C2) within the mini-box corer was low (less than 12%) based on the replicate core data, with only a few exceptions. One station (CS126) had consistently higher CV's for most parameters than at the other three stations although they were still low and ranged from 4% to 23%. The CVs for all parameters at station CS164, CS167 and CS135 were less than 12% with only one exception at station CS164 where the CV for lead was 23% and at station CS167 where the CV for mercury was 18%. This suggests that variability in sediment quality within the mini-box corer was low but did vary between stations and with the parameter. Mercury and lead had the highest within box core variability.

Unlike the other QA/QC stations, samples collected from station C135 were a combination of one single sample and two additional samples that were each split into three sub-samples. Hence the CV for each parameters was calculated by two different methods. The CV was determined based on a mean that was calculated by using the first sample from each split sample and the third replicate (which was a single sample) as well as by using the mean from each split sample combined with the third replicate single sample. In both cases the CV for all parameters were almost identical, and with only one exception all CVs were less than 10%. These results, overall, suggest that the mini-box corer was a useful tool to accommodate a sampling design that required several samples from a single site since variability within the box was low. As well, the results suggest that for most parameters individual samples collected from the mini-box corer adequately described the sampling device without replication.

Variability for almost all parameters was low within split samples (station CS135) suggesting that the samples were well mixed prior to distribution among sample jars (Appendix C2). Based on laboratory QA/QC information some variability between split samples may be due to analytical error. The CVs for the two split samples for all parameters ranged from 1 to 21% with values for most parameters less than 10%. The highest variability was associated with total phosphorus and lead for both split samples and with zinc (14%) for one split while the other split had a CV for zinc of only 5%.

Within station variability was assessed by comparing the concentration of the parameter in the routine sample core with the mean and 95% upper and lower confidence intervals generated for the three replicate samples from the QA/QC mini-box core (Appendix C3i & C3ii). Comparisons were made using both particle size corrected and uncorrected data. Results were similar using both data sets since particle size differences between samples at any one station were low. Because the sample size was small ( $n=3$ ), a t-test would have produced results with a predisposition to accepting the null hypothesis since the power of the test would have been low.

Results from the comparison between the routine stations with the QA/QC samples suggest some variability of contaminant concentrations within a station (particularly for total phosphorus and to a lesser extent for lead), but typically the difference in concentrations were not large. For most parameters the concentrations for the routine samples tended to be within the upper and lower confidence bands generated for the QA/QC samples. Samples which fell outside the confidence bands were not sufficiently different to be environmentally significant (i.e. the difference in concentration in almost all cases did not change the designation of whether the sample was above

of below the sediment quality guidelines). Variability within these stations appears to be low suggesting that single samples adequately represent a site. A review of the station's northing and easting for the QA/QC samples (Appendix A) show that QA/QC stations CS164 and CS167 were fairly close to the original samples.

For station CS126 the QA/QC station location difference was about 5.5 m east and 7 m south of the original site, possibly providing an explanation for the higher variability in contaminant concentrations observed at that station relative to the other QA/QC sites. The confidence bands generated for this station were also wide due to the high variability within the mini-box. Relatively high variability within the box and within the site suggest that this area may have a patchy sediment quality.

For QA/QC station CS135 mercury concentrations were only provided for the single replicate samples. However, the samples collected for the EC/MOE interlaboratory comparison were also collected from the same mini-box as the QA/QC samples which, therefore, essentially provided an additional replicate for the QA/QC mini-box drop. The mercury concentration in the single replicate was 11.3  $\mu\text{g/g}$  while the concentration in the interlab comparison sample was 9.41  $\mu\text{g/g}$ . Both concentrations were high compared with the mercury concentration in the routine sample (3.75  $\mu\text{g/g}$ ). Information on the exact location of the QA/QC sample was not available to determine the distance between each drop of the mini-box corer. Speculation on within site variability for Hg at this station is therefore not possible.

In general, for the four QA/QC stations, there was good agreement for all parameters between the EC samples from the interlaboratory comparison with the three replicates collected for QA/QC analysis (Appendix E).

**APPENDIX C(1):** The expected mean squares generated by the ANOVA using non-transformed data were used to calculate the variance components associated with the between station variability and within station variability. The percent variability within each component was calculated relative to the "total" variability based on the total variance component.

	Variance Component	Percent Variability		Variance Component	Percent Variability
Aluminum			Nickel		
Total	3628438.907		Total	12.740	
STN	2870641.657	79	STN	7.885	62
REP(STN)	757797.250	21	REP(STN)	4.855	38
Cadmium			Lead		
Total	0.048		Total	4387.637	
STN	0.043	91	STN	4005.757	91
REP(STN)	0.004	9	REP(STN)	381.880	9
Chromium			Zinc		
Total	29.895		Total	46366.380	
STN	15.750	53	STN	45650.630	98
REP(STN)	14.144	47	REP(STN)	715.750	2
Copper			Total Phosphorus		
Total	174.146		Total	2836.361	
STN	163.586	94	STN	856.528	30
REP(STN)	10.559	6	REP(STN)	1979.833	70
Iron			TOC		
Total	766211.130		Total	1.200	
STN	375088.880	49	STN	1.171	98
REP(STN)	391122.250	51	REP(STN)	0.028	2
Manganese			Mercury		
Total	293.565		Total	17.128	
STN	60.481	21	STN	15.594	91
REP(STN)	233.083	79	REP(STN)	1.534	9

**APPENDIX C(2):** Metal and nutrient concentrations from three stations (CS126, CS164, CS167) where replicate cores were collected from a single box core to investigate within station variability. Metal and nutrient concentrations from station CS135 where two samples were split into three subsamples to investigate within sample variability. Mean/SD and CV for stn CS135 is based on the single core sample and the mean of each split sample.

Station		Aluminum mg/Kg	Cadmium mg/Kg	Chromium mg/Kg	Copper mg/Kg	Iron mg/Kg	Mercury mg/Kg	Manganese mg/Kg	Nickel mg/Kg	Lead mg/Kg	Zinc mg/Kg	Phosphorus (Total) mg/Kg	Total Organic Carbon %	Silt+Clay %
CS126	Mean	13466.67	0.59	32.43	31.63	16133.33	9.16	285.33	21.33	34.43	189.67	674.00	4.75	46.93
	S.D.	1457.166	0.072	7.047	3.557	923.760	2.096	26.633	4.055	3.717	39.425	26.058	0.328	4.038
	C.V. (%)	11	12	22	11	6	23	9	19	11	21	4	7	9
CS164	Mean	15600.00	1.01	42.70	59.70	16033.33	3.46	271.67	27.73	164.67	597.67	616.00	2.58	75.90
	S.D.	754.983	0.056	2.606	5.311	723.418	0.411	10.116	1.419	38.682	35.726	26.851	0.067	3.341
	C.V. (%)	5	6	6	9	5	12	4	5	23	6	4	3	4
CS167	Mean	17666.67	1.06	36.10	33.53	17266.67	1.05	265.33	27.77	33.13	108.33	685.00	2.84	75.43
	S.D.	152.753	0.015	0.346	0.839	251.661	0.194	6.658	0.808	2.155	2.082	77.698	0.006	3.646
	C.V. (%)	1	1	1	3	1	18	3	3	7	2	11	0	5
CS135	Mean	16433.33	0.93	33.99	38.09	15600.00	ND	290.67	26.79	41.30	284.11	707.22	2.41	67.73
	S.D.	560.753	0.092	0.096	0.815	352.767	ND	8.838	0.560	3.571	5.168	21.859	0.026	0.404
	C.V. (%)	3	10	0	2	2		3	2	9	2	3	1	1
Within sample variability														
CS135-2	Mean	16633.33	0.87	33.93	38.27	15866.67	ND	298.33	26.67	42.97	280.33	720.67	2.40	67.50
	S.D.	1101.514	0.066	2.650	3.894	873.689	ND	15.885	1.677	5.764	39.145	153.106	0.328	3.831
	C.V. (%)	7	8	8	10	6	ND	5	6	13	14	21	14	6
CS135-3	Mean	16866.67	1.04	33.93	38.80	15733.33	ND	292.67	27.40	43.73	290.00	682.00	2.43	67.50
	S.D.	1069.268	0.221	1.210	2.330	665.833	ND	22.030	0.954	4.960	15.100	77.582	0.073	3.251
	C.V. (%)	6	21	4	6	4	ND	8	3	11	5	11	3	5

ND = No data

APPENDIX C(3): Sediment concentrations (ug/g dry wt.) in QA/QC samples compared with concentrations in routine samples collected from the same stations. St. Lawrence River, Cornwall, Ontario, 1997. a = 0.05. All data corrected for particle size.

Station	Al corr	Cd corr	Cr corr	Cu corr	Fe corr	Hg corr	Mn corr	Ni corr	Pb corr	Zn corr	TP corr	TOC corr
QA/QC CS126-1	21783	1.012	46.8	54.8	24100	17.46	420	32.6	59.8	358	1003	7.361
QA/QC CS126-2	17464	0.756	39.5	42.2	23088	13.42	397	25.8	48.4	228	1037	7.510
QA/QC CS126-3	25247	1.036	70.2	53.8	29948	12.38	550	44.4	55.5	319	1170	7.693
Mean	21498	0.935	52.2	50.3	25712	14.42	456	34.2	54.6	302	1070	7.521
Standard Deviation	3999	0.155	16.0	7.0	3703	2.68	83	9.4	5.8	67	88	0.166
CI	9687	0.385	39.8	17.5	9200	6.66	205	23.4	14.3	166	219	0.412
95% Upper Confidence Interval	31184	1.320	91.9	67.7	34912	21.08	661	57.7	68.9	468	1290	7.933
95% Lower Confidence Interval	11811	0.550	12.4	32.8	16513	7.76	250	10.8	40.3	136	851	7.109
CS126	17381	1.300	43.0	48.0	22922	9.39	363	34.5	45.5	226	825	5.552
Station	Al corr	Cd corr	Cr corr	Cu corr	Fe corr	Hg corr	Mn corr	Ni corr	Pb corr	Zn corr	TP corr	TOC corr
QA/QC CS164-1	15187	1.035	40.0	58.1	15864	3.14	268	25.3	180.9	566	610	2.565
QA/QC CS164-2	15288	0.907	42.9	60.8	15475	3.69	261	26.3	175.4	598	593	2.413
QA/QC CS164-3	15148	1.004	42.0	55.5	15557	3.27	266	29.7	122.8	583	599	2.578
Mean	15208	0.982	41.6	58.1	15632	3.36	265	27.1	159.7	583	601	2.519
Standard Deviation	72	0.067	1.4	2.7	205	0.28	4	2.3	32.1	16	9	0.092
CI	179	0.166	3.6	6.6	509	0.71	9	5.7	79.6	40	22	0.228
95% Upper Confidence Interval	15387	1.148	45.2	64.7	16141	4.07	274	32.8	239.3	623	623	2.747
95% Lower Confidence Interval	15028	0.816	38.1	51.5	15123	2.66	256	21.4	80.1	542	578	2.291
CS164	16676	0.926	50.8	62.4	18448	3.19	304	26.0	141.7	697	883	2.558
Station	Al corr	Cd corr	Cr corr	Cu corr	Fe corr	Hg corr	Mn corr	Ni corr	Pb corr	Zn corr	TP corr	TOC corr
QA/QC CS167-1	16455	0.978	33.8	32.4	15985	1.03	245	26.8	31.9	102	722	2.663
QA/QC CS167-2	17212	1.040	35.5	32.1	16823	1.19	255	26.2	33.8	107	654	2.766
QA/QC CS167-3	18422	1.097	37.2	34.3	18112	0.87	283	28.9	31.8	110	635	2.934
Mean	17363	1.038	35.5	32.9	16973	1.03	261	27.3	32.5	106	671	2.788
Standard Deviation	992	0.060	1.7	1.2	1072	0.16	19	1.4	1.2	4	46	0.137
CI	2465	0.148	4.2	2.9	2662	0.39	48	3.5	2.9	9	113	0.340
95% Upper Confidence Interval	19828	1.187	39.7	35.8	19635	1.42	309	30.8	35.4	115	784	3.128
95% Lower Confidence Interval	14898	0.890	31.2	30.0	14311	0.64	213	23.7	29.6	97	557	2.447
CS167	17243	0.934	38.0	40.7	16730	1.22	272	30.7	37.6	110	890	3.048
Station	Al corr	Cd corr	Cr corr	Cu corr	Fe corr	Hg corr	Mn corr	Ni corr	Pb corr	Zn corr	TP corr	TOC corr
QA/QC CS135-1	17144	0.967	37.0	40.4	16493	12.26	305	28.5	40.4	306	780	2.589
QA/QC CS135-2	18810	0.926	37.3	41.3	18134		346	29.1	43.5	297	766	2.485
QA/QC CS135-3	18109	0.988	37.4	40.5	17215		315	29.5	43.1	309	665	2.667
Mean	18021	0.960	37.2	40.7	17280	12.26	322	29.0	42.3	304	737	2.580
Standard Deviation	837	0.032	0.2	0.5	823		21	0.5	1.7	6	63	0.092
CI	2078	0.079	0.6	1.3	2043		53	1.2	4.2	15	156	0.227
95% Upper Confidence Interval	20099	1.039	37.8	42.1	19324		375	30.2	46.6	318	893	2.808
95% Lower Confidence Interval	15943	0.882	36.7	39.4	15237		269	27.8	38.1	289	581	2.353
CS135	21048	1.090	44.6	50.4	20494	4.15	367	25.4	65.1	259	731	2.335

**APPENDIX C(III):** Sediment concentrations ( $\mu\text{g/g dry wt.}$ ) in QA/QC samples compared with concentrations in routine samples collected from the same stations.  
St. Lawrence River, Cornwall, Ontario, 1997.  $\alpha = 0.05$

Station	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	TP	TOC	Sand	Silt	Clay
QA/QC CS126-1	14100	0.655	30.3	35.5	15600	11.30	272	21.1	38.7	232	649	4.765	52.1	31.9	16.0
QA/QC CS126-2	11800	0.511	26.7	28.5	15600	9.07	268	17.4	32.7	154	701	5.074	49.6	30.0	20.0
QA/QC CS126-3	14500	0.595	40.3	30.9	17200	7.11	316	25.5	31.9	183	672	4.418	57.6	29.5	13.0
Mean	13467	0.59	32.4	31.6	16133	9.16	285	21.3	34.4	190	674	4.752	53.1	30.5	16.3
Standard Deviation	1457	0.07	7.0	3.6	924	2.10	27	4.1	3.7	39	26	0.328	4.1	1.3	3.5
CI	3620	0.180	17.5	8.8	2295	5.21	66	10.1	9.2	98	65	0.815	10.2	3.1	8.7
95% Upper Confidence Interval	17086	0.767	49.9	40.5	18428	14.37	351	31.4	43.7	288	739	5.568	63.3	33.6	25.1
95% Lower Confidence Interval	9847	0.407	14.9	22.8	13839	3.95	219	11.3	25.2	92	609	3.937	42.9	27.3	7.6
CS126	9630	0.720	23.8	26.6	12700	5.20	201	19.1	25.2	125	457	3.076	58.3	30.5	10.5

Station	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	TP	TOC	Sand	Silt	Clay
QA/QC CS164-1	15700	1.070	41.4	60.1	16400	3.25	277	26.2	187.0	585	631	2.652	23.5	58.8	17.7
QA/QC CS164-2	16300	0.967	45.7	64.8	16500	3.93	278	28.0	187.0	638	632	2.573	21.0	66.1	12.8
QA/QC CS164-3	14800	0.981	41.0	54.2	15200	3.19	260	29.0	120.0	570	585	2.519	26.4	57.3	15.0
Mean	15600	1.006	42.7	59.7	16033	3.46	272	27.7	164.7	598	616	2.581	23.6	60.7	15.2
Standard Deviation	755	0.056	2.6	5.3	723	0.41	10	1.4	38.7	36	27	0.067	2.7	4.7	2.5
CI	1875	0.139	6.5	13.2	1797	1.02	25	3.5	96.1	89	67	0.166	6.7	11.7	6.1
95% Upper Confidence Interval	17475	1.145	49.2	72.9	17830	4.48	297	31.3	260.8	686	683	2.747	30.3	72.4	21.3
95% Lower Confidence Interval	13725	0.887	36.2	46.5	14238	2.44	247	24.2	68.6	509	549	2.415	16.9	49.0	9.1
CS164	16000	0.888	48.7	59.9	17700	3.06	292	24.9	136.0	669	847	2.454	29.0	53.6	17.4

Station	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	TP	TOC	Sand	Silt	Clay
QA/QC CS167-1	17500	1.040	35.9	34.5	17000	1.10	261	28.5	33.9	109	768	2.832	21.3	63.4	15.3
QA/QC CS167-2	17700	1.070	36.5	33.0	17300	1.22	262	26.9	34.8	110	673	2.844	23.9	61.5	14.6
QA/QC CS167-3	17800	1.060	35.9	33.1	17500	0.84	273	27.9	30.7	106	614	2.835	28.5	56.0	15.5
Mean	17667	1.057	36.1	33.5	17267	1.05	265	27.8	33.1	108	685	2.837	24.6	60.3	15.1
Standard Deviation	153	0.015	0.3	0.8	252	0.19	7	0.8	2.2	2	78	0.006	3.6	3.8	0.5
CI	379	0.038	0.9	2.1	625	0.48	17	2.0	5.4	5	193	0.016	9.1	9.5	1.2
95% Upper Confidence Interval	18046	1.095	37.0	35.6	17892	1.54	282	29.8	38.5	114	878	2.853	33.6	69.8	16.3
95% Lower Confidence Interval	17287	1.019	35.2	31.5	16642	0.57	249	25.8	27.8	103	492	2.821	15.5	50.8	14.0
CS167	16800	0.910	37.0	39.7	16300	1.19	265	29.9	36.6	107	867	2.970	27.9	51.6	20.5

Station	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	TP	TOC	Sand	Silt	Clay
QA/QC CS135-1	15800	0.891	34.1	37.2	15200	11.30	281	26.3	37.2	282	719	2.386	31.8	49.5	18.7
QA/QC CS135-2	16700	0.822	33.1	36.7	16100		307	25.8	38.6	264	680	2.206	34.4	49.1	16.6
QA/QC CS135-3	16200	0.884	33.5	36.2	15400		282	26.4	38.6	276	595	2.386	33.8	51.4	14.8
Mean	16233	0.868	33.6	36.7	15567	11.30	290	26.2	38.1	274	665	2.326	33.3	50.0	16.7
Standard Deviation	451	0.038	0.5	0.5	473		15	0.3	0.8	9	63	0.104	1.4	1.2	2.0
CI	1120	0.094	1.3	1.2	1174		37	0.8	2.0	23	158	0.258	3.4	3.1	4.8
95% Upper Confidence Interval	17353	0.960	34.8	37.9	16741		327	27.0	40.1	297	822	2.584	36.7	53.1	21.5
95% Lower Confidence Interval	15113	0.771	32.3	35.5	14393		253	25.4	36.1	251	507	2.068	30.0	46.9	11.9
CS135	19000	0.984	40.3	45.5	18500	3.75	331	22.9	58.8	234	660	2.108	33.2	44.9	21.9

\*\*value from single sample

**APPENDIX C(4): QA/QC Sampling. Metal and total phosphorus concentrations (Mg/Kg dry weight), % TOC and particle size distribution in sediment samples (top 10 cm core sample) collected from the St. Lawrence River, 1997**

Station	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	TP	TOC	Sand	Silt	Clay
Replicate core samples	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	Mg/Kg	%	%	%	%
CS126-1	14100	0.655	30.3	35.5	15600	11.30	272	21.1	38.7	232	649	4.765	52.1	31.9	16.0
CS126-2	11800	0.511	26.7	28.5	15600	9.07	268	17.4	32.7	154	701	5.074	49.6	30.0	20.0
CS126-3	14500	0.595	40.3	30.9	17200	7.11	316	25.5	31.9	183	672	4.418	57.6	29.5	13.0
CS164-1	15700	1.070	41.4	60.1	16400	3.25	277	26.2	187.0	585	631	2.652	23.5	58.8	17.7
CS164-2	16300	0.967	45.7	64.8	16500	3.93	278	28.0	187.0	638	632	2.573	21.0	66.1	12.8
CS164-3	14800	0.981	41.0	54.2	15200	3.19	260	29.0	120.0	570	585	2.519	26.4	57.3	15.0
CS167-1	17500	1.040	35.9	34.5	17000	1.10	261	28.5	33.9	109	768	2.832	21.3	63.4	15.3
CS167-2	17700	1.070	36.5	33.0	17300	1.22	262	26.9	34.8	110	673	2.844	23.9	61.5	14.6
CS167-3	17800	1.060	35.9	33.1	17500	0.84	273	27.9	30.7	106	614	2.835	28.5	56.0	15.5
CS135-1	15800	0.891	34.1	37.2	15200	11.30	281	26.3	37.2	282	719	2.386	31.8	49.5	18.7
Within sample splits															
CS135-2	16700	0.822	33.1	36.7	16100		307	25.8	38.6	264	680	2.206	34.4	49.1	16.6
CS135-2	15500	0.834	31.8	35.4	14900		280	25.6	40.8	252	592	2.209	35.1	47.8	17.1
CS135-2	17700	0.941	36.9	42.7	16600		308	28.6	49.5	325	890	2.776	28.1	53.7	18.2
CS135-3	16200	0.884	33.5	36.2	15400		282	26.4	38.6	276	595	2.386	33.8	51.4	14.8
CS135-3	16300	0.936	33.0	39.5	15300		278	28.3	48.5	288	707	2.399	35.0	45.0	20.1
CS135-3	18100	1.290	35.3	40.7	16500		318	27.5	44.1	306	744	2.519	28.8	50.7	20.5

**APPENDIX D:** Component loadings and percent of total variance explained for the PCA of sediment quality in the St. Lawrence River, 1997.

Log Transformed Data - using only percent silt

	PC I	PC II	PC III
Aluminum	0.952	-0.151	0.06
Cadmium	0.84	0.293	-0.028
Chromium	0.961	0.179	0.138
Copper	0.644	0.714	0.005
Iron	0.912	-0.3	0.014
Mercury	-0.601	0.658	-0.216
Manganese	0.793	-0.438	0.065
Nickel	0.93	0.011	-0.034
Phosphorus	0.799	-0.308	0.178
Lead	0.151	0.918	0.271
Zinc	0.21	0.923	0.145
TOC	0.486	0.175	-0.831
Silt	0.872	0.115	-0.163

Percent of total variance explained

56%      81%      88%

**APPENDIX E:** Data from the MOE and EC interlaboratory comparison.

**MOE SPLIT SAMPLE DATA**

Station Number (EC Station Description)	MOE Station Description	MOE Field Sample No.	Aluminum mg/Kg	Cadmium mg/Kg	Chromium mg/Kg	Copper mg/Kg	Iron mg/Kg	Mercury mg/Kg	Manganese0 mg/Kg	Nickel mg/Kg	Lead mg/Kg	Zinc mg/Kg	SUM1 Clay	SUM2 Silt	SUM3 Sand
CS167-SPLIT	194	GL778804	12000	1.6	35	41	18000	0.83	250	25	36	130	14.0	44	42
CS181-SPLIT	199	GL778802	15000	1.4	38	37	22000	0.10	390	28	32	130	17.9	40	42
CS168-SPLIT	195	GL778803	8300	1.2	28	38	14000	1.50	210	23	36	100	9.3	36	55
CS171-SPLIT	197	GL778801	10000	1.0	28	30	16000	0.26	300	21	29	120	14.5	35	50
CS105-SPLIT	162	GL778805	13000	1.4	44	61	20000	1.40	300	28	76	710	20.7	58	21
CS164-SPLIT	192	GL778806	11000	1.2	46	75	16000	2.40	270	25	170	780	17.4	52	30
CS135-SPLIT	157	GL778808	11000	1.3	36	57	16000	5.80	300	24	51	400	26.3	60	13
CS126-SPLIT	183	GL778809	8900	1.0	31	39	16000	5.50	280	22	38	210	15.9	52	32

**EC SPLIT SAMPLE DATA**

Station Number (EC Station Description)	Aluminum mg/Kg	Cadmium mg/Kg	Chromium mg/Kg	Copper mg/Kg	Iron mg/Kg	Mercury mg/Kg	Manganese mg/Kg	Nickel mg/Kg	Lead mg/Kg	Zinc mg/Kg	SUM1 Clay	SUM2 Silt	SUM3 Sand
CS167-SPLIT	20400	1.160	42.3	37.9	19800	0.74	290	30.0	38.1	125	20.1	54.3	25.7
CS181-SPLIT	22400	0.984	41.7	33.6	21400	0.14	381	30.7	29.6	112	25.0	60.9	14.0
CS168-SPLIT	15000	0.598	36.1	33.1	15700	1.18	266	24.3	33.2	101	15.7	39.4	44.9
CS171-SPLIT	16500	0.719	33.1	29.8	17000	0.37	310	23.4	25.5	109	18.3	37.7	43.9
CS105-SPLIT	19000	1.020	43.4	45.7	18400	1.95	286	26.0	69.7	581	21.6	68.6	9.8
CS164-SPLIT	15300	0.993	44.9	55.3	15900	2.80	269	25.1	135.0	620	15.7	50.3	33.2
CS135-SPLIT	19100	0.948	40.2	45.7	17000	9.41	315	26.3	46.1	345	22.3	43.3	34.4
CS126-SPLIT	12000	0.615	26.7	37.0	14800	6.30	260	18.1	29.4	142	11.0	26.0	62.6



